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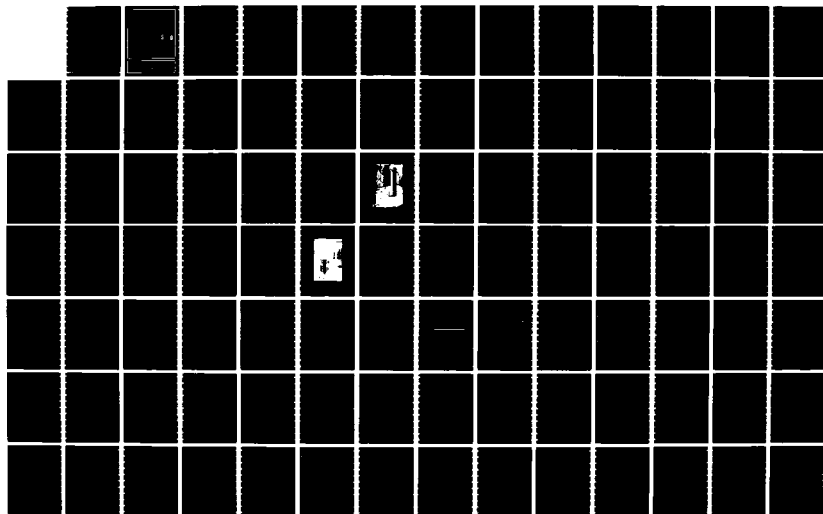
DIESEL FUEL PROCESSING FOR THE PAFC PROCESS  
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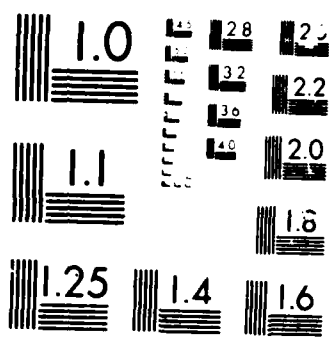
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DIESEL FUEL PROCESSING FOR THE PAFC  
PROCESS DEMONSTRATION

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15 DECEMBER 1986

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FINAL TECHNICAL REPORT  
For Period 26 August 1985 - 15 July 1986

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Prepared For:

BELVOIR RESEARCH, DEVELOPMENT AND ENGINEERING CENTER  
DIRECTORATE FOR LOGISTICS SUPPORT  
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1.0 SUMMARY

This final report describes ERC's approach, equipment and results from the 400-hour fuel processor demonstration test. This test demonstrated the production of fuel cell grade hydrogen from diesel fuel.

All process goals have been achieved, including the overall efficiency of hydrogen production.

This report presents descriptions of key components, process flow and material balance for the process demonstration. In addition, test data and results are described.

The subscale demonstration equipment processed diesel fuel at a rate of 1.15 lbs/hr, which represents about 2.5 kW fuel cell power.

The 400-hour process demonstration test consisted of a 300 hour period in which the test unit operated in daily cycles of 15-16 hours. During this period, sulfur levels to the reformer were higher than anticipated, and caused a gradual sulfur poisoning of the reformer. This was corrected by a regeneration of the reformer, and replacement of the HDS catalyst. The remaining portion of the test (106 hours) was conducted in a continuous manner (with one weekend shutdown). The sulfur level to the reformer was maintained below 1 ppm, and stable operation was obtained with full conversion of fuel and no evidence of carbon or gum formation.

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## 2.0 INTRODUCTION

The objective of this effort was to demonstrate a fuel processor capable of producing hydrogen rich gas from diesel fuel. The product gas must be suitable for a phosphoric acid fuel cell. The quality of the gas produced must meet the criteria outlined below:

- $H_2$  = 50% or greater by volume (dry basis)
- CO = 1% or less by volume (dry basis)
- S = 10 WPPM or less
  
- Hydrogen Production: 0.365 lb  $H_2$ /lb fuel consumed minimum  
0.42 lb  $H_2$ /lb fuel consumed desired

In order to attain this objective, a process was demonstrated in a 400 hour test. This test was intended to generate sufficient data to determine feasibility of the process.

The ERC process demonstration is based on pressurized desulfurization of the fuel followed by conventional reforming and shifting of the low sulfur diesel fuel. The desulfurization consists of two stage HDS/ZnO in which the ZnO is regenerable.

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### 3.0 APPROACH

The approach chosen by ERC is based on front end desulfurization of the fuel prior to reforming, as is done commercially with lighter hydrocarbons. By desulfurizing the fuel before the reformer, it is possible to use conventional reforming technology, and use temperatures of 900-1300°F in the reformer. The moderate temperatures allow the use of less exotic materials in the construction of the reformer. In addition, the hydrodesulfurization process also hydrotreats the fuel reducing the olefin and aromatic content and lowers the carbon formation tendency in the reformer. Following the hydrodesulfurization, a regenerable zinc oxide reactor is planned. By regenerating the zinc oxide, a suitable sized reactor can be chosen, and replacement of sulfided ZnO is not necessary at frequent time intervals. Figure 3.0 depicts a block diagram of the approach described above.

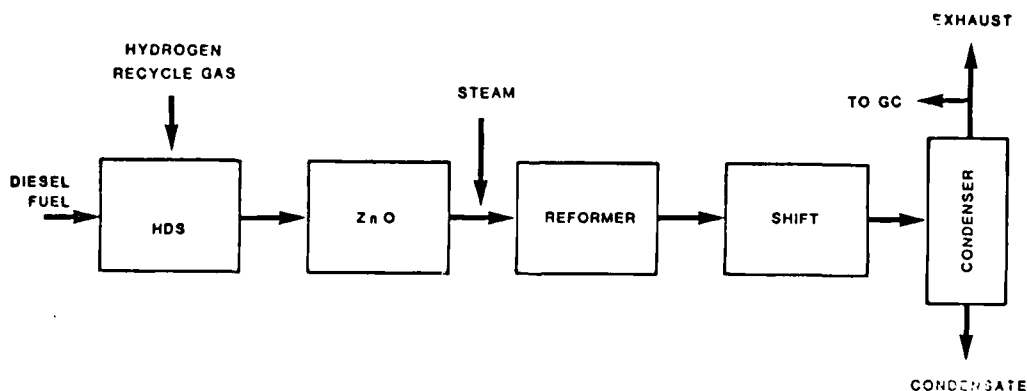


FIGURE 3.0A  
DIESEL FUEL REFORMING PROCESS DEMONSTRATION  
CONCEPTUAL BLOCK DIAGRAM

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#### 4.0 BACKGROUND

The processing of heavy hydrocarbons to fuel cell grade hydrogen is a challenge due to two primary factors:

- sulfur in the fuel
- carbon formation

Sulfur in the fuel poisons or deactivates reforming and shift catalysts, and ultimately deactivates fuel cell catalysts if allowed to reach the fuel cell. Carbon and gum formation is another potential hazard when processing heavy hydrocarbons, particularly when the aromatic content is high. Carbon and gum formation can deactivate catalysts and plug up a reactor in an extreme condition.

In the past, efforts have been directed towards developing sulfur tolerant catalyst which can operate in the presence of sulfur. These systems are based on a low activity calcium based catalyst or other non-conventional catalysts. This allows reforming in the presence of sulfur but requires larger catalyst volumes than conventional reforming due to the reduced activity of the sulfur tolerant catalyst. In addition, higher temperatures (1600-1900°F) are required to overcome the lower activity in the presence of sulfur. The cracking reactions of higher hydrocarbons to polymers and to coke are more pronounced at elevated temperatures, so that the risk of carbon formation is increased at elevated temperatures. In this type of system, the organic sulfur compounds in the fuel are thermally decomposed to H<sub>2</sub>S in the high temperature reformer and removed by a sulfur sorbent such as zinc oxide after the reformer. Due to the reduced activity of this type of catalyst, a secondary reformer is generally required in order to complete conversion. Although high temperature sulfur tolerant reforming is potentially attractive, a viable system has not been demonstrated to date, partly due to the factors mentioned above.

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The utilization of logistic fuels in fuel cell power plants has been hampered by the lack of a demonstrated fuel processor capable of operating on these fuels. This effort was conducted to demonstrate such a process. Logistic fuels specified for this program include DF-2, DF-A and JP-4. Due to time limitations of the program, the heaviest fuel, DF-2, was chosen for the demonstration test. Typical properties of DF-2 are shown in Table 4.0.

TABLE 4.0  
DIESEL FUEL PROPERTIES

DIESEL FUEL FORMULA:	C <sub>15.2</sub> H <sub>27.7</sub>
DIESEL FUEL MOLECULAR WEIGHT:	210
H/C RATIO:	1.82
API GRAVITY:	35
BOILING POINT RANGE:	334°F - 646°F
SULFUR:	0.28 wt%

## 5.0 KEY COMPONENTS

The diesel fuel processor consists of the following key components:

- hydrodesulfurizer
- zinc oxide
- reformer
- shift

Diesel fuel is pumped into the hydrodesulfurizer together with a hydrogen containing recycle stream which has been preheated. The hydrogen recycle stream is simulated and preheated in the process demonstration, but would normally be obtained from the power plant system. Sulfur compounds in the diesel fuel are converted to hydrogen sulfide at 650 psig pressure in the HDS (hydrodesulfurizer). The high pressure is required in the HDS in order to obtain high activity of the catalyst and to minimize decay due to carbon formation. The pressure is reduced to 1 atmosphere after the HDS and a vaporizer is used to vaporize the desulfurized diesel fuel. Prior to this pressure reduction the bulk of the diesel fuel in the HDS is in liquid form. The hydrogen sulfide is then removed in a zinc oxide reactor. The desulfurized, hydrotreated fuel is then reformed with the addition of steam, and the product gas is cooled and shifted in a low temperature shift reactor. Gas leaving the shift reactor is cooled to remove water and is analyzed by gas chromatography. A summary of the baseline operating conditions is shown in Table 5.0A. The flows used during the process demonstration are equivalent to 2.5 kW rated flow.

The catalysts used for HDS, reforming and shift are manufactured by Haldor Topsoe A/S and are identified by their commercial designation. The Zinc Oxide sorbent used is also manufactured by Haldor Topsoe A/S and is identified by its commercial designation. Table 5.0B summarizes the catalysts used.

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Process instrumentation measuring temperatures, pressures and flows is shown in Figure 5.0. HDS, ZnO and shift reactors were instrumented to measure bed temperatures at inlet, mid-bed and exit of each reactor. The reformer was instrumented to measure process gas at reformer inlet, catalyst bed exit, and reformer exit. In addition, several wall temperatures of the catalyst section and regenerative section were measured, as shown.

TABLE 5.0A  
PROCESS DEMONSTRATION BASELINE OPERATION CONDITION

HDS Operating Pressure:	650 psig
Reformer Operating Pressure:	12 psig inlet
HDS Exit Temperature:	700°F
ZnO Exit Temperature:	700°F
Reformer Inlet Temperature:	950°F
Reformer Exit Temperature:	1300°F
Shift Reactor Inlet:	400°F
Shift Reactor Exit:	400°F
H <sub>2</sub> O/C at Reformer Inlet:	5.5



TABLE 5.0B  
CATALYSTS USED AND THEIR DESIGNATIONS

REACTOR	CATALYST MANUFACTURER	CATALYST DESIGNATION	SIZE
HDS	HALDOR TOPSOE	TK-551	1/32" Extrusions
REFORMER	HALDOR TOPSOE	RKNR	4.5 x 4.5 mm Tablets
SHIFT	HALDOR TOPSOE	LK-801	4.3 x 3.2 mm Pellets
ZNO	HALDOR TOPSOE	HTZ-3	3 mm Extrusions

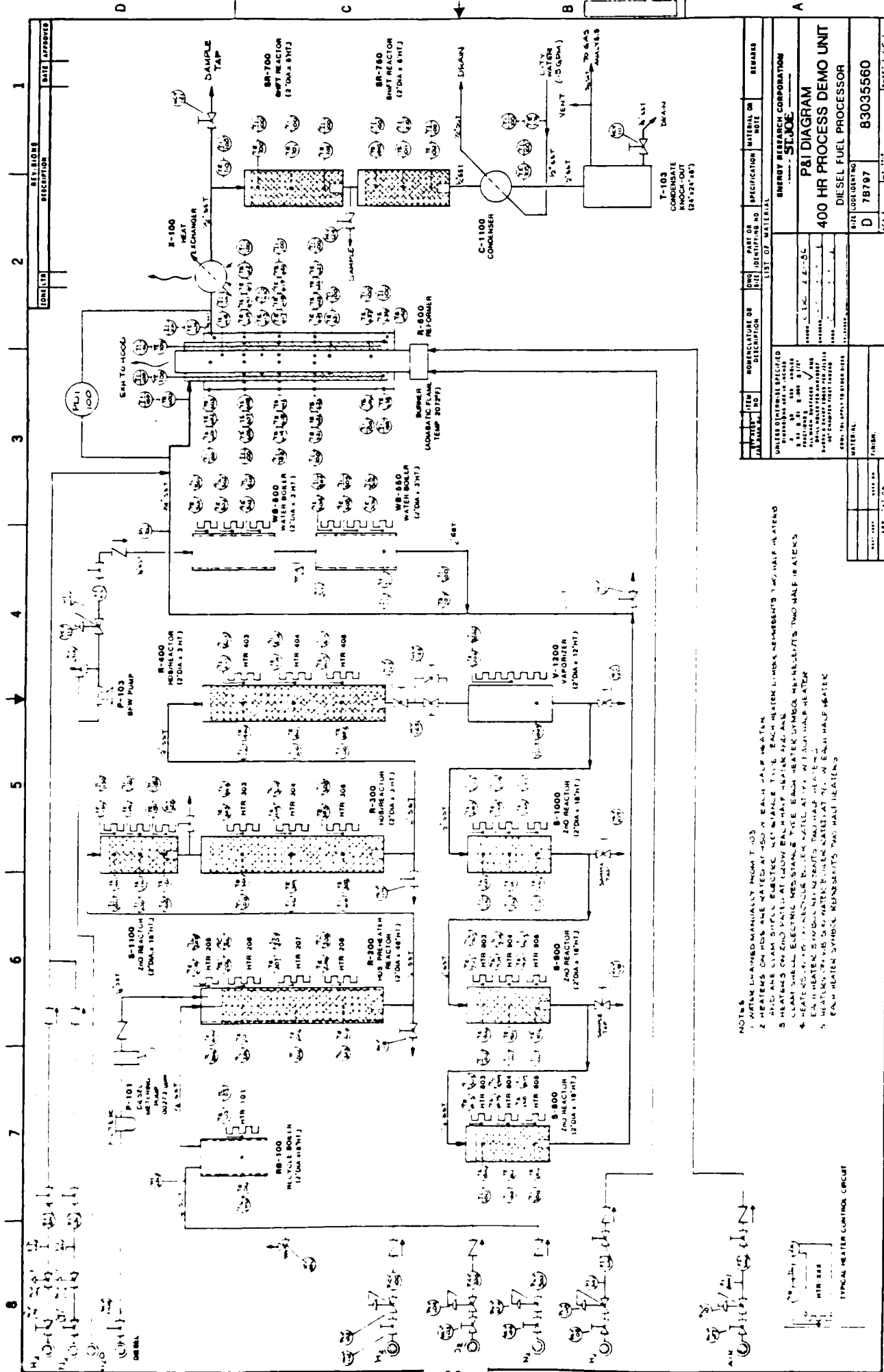


FIGURE 5.8 Process and Instrument Diagram

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### 5.1 SULFUR REMOVAL

Desulfurization of the fuel is accomplished by a 2 stage high pressure desulfurization over an HDS catalyst in the presence of hydrogen recycle gas followed by absorption of the  $H_2S$  by  $ZnO$ . The  $ZnO$  is designed to be regenerable and therefore can be sized as desired depending on the regeneration frequency. The sulfur removal system is designed to lower the sulfur level to  $<1$  wppm in the fuel in order to maintain high activity in the reformer.

#### 5.1.1 Hydrodesulfurizer

The hydrodesulfurizer system consists of three HDS reactors. The first reactor serves to preheat and partially vaporize the fuel and recycle gas mixture and desulfurize the fuel in the first stage. The second and third HDS reactors serve to provide additional catalyst volume for a second stage desulfurization. Table 5.1.1 summarizes the key features of the HDS reactors. Figure 5.1.1 depicts the configuration of the two stage HDS system, as well as the steam addition required for reforming.

#### 5.1.2 Zinc Oxide

The zinc oxide reactors are designed to remove the  $H_2S$  generated in the HDS reactors thereby rendering the processed fuel low in sulfur. The reaction in the  $ZnO$  reactor is as follows:



This reaction is limited by the equilibrium that is established between the  $H_2O$  and the  $H_2S$  at the reactor exit, as shown in Figure 5.1.2. Pressure does not affect this equilibrium. Lower temperatures and low  $H_2O$  levels favor low  $H_2S$  levels at the exit of the reactor.

The key features of the  $ZnO$  reactors are summarized in Table 5.1.2. The first zinc oxide reactor was replaced with fresh  $ZnO$

TABLE 5.1.1.1  
HDS UNITS

REACTOR NUMBER	R-200	R-300	R-400
Material of Construction	316 SS	316 SS	316 SS
Dimensions	2" diam x 46" length	2" diam x 36" length	2" diam x 36" length
Construction	sch. 40 pipe	sch. 40 pipe	sch. 40 pipe
Catalyst	TK 551	TK 551	TK 551
Reactant Feed Rate:			
Fuel	1.15 lb/hr	1.15 lb/hr	1.15 lb/hr
Hydrogen	.06 lb/hr	.06 lb/hr	.06 lb/hr
Temperature	700°F	700°F	700°F
Pressure	650 psig	650 psig	650 psig

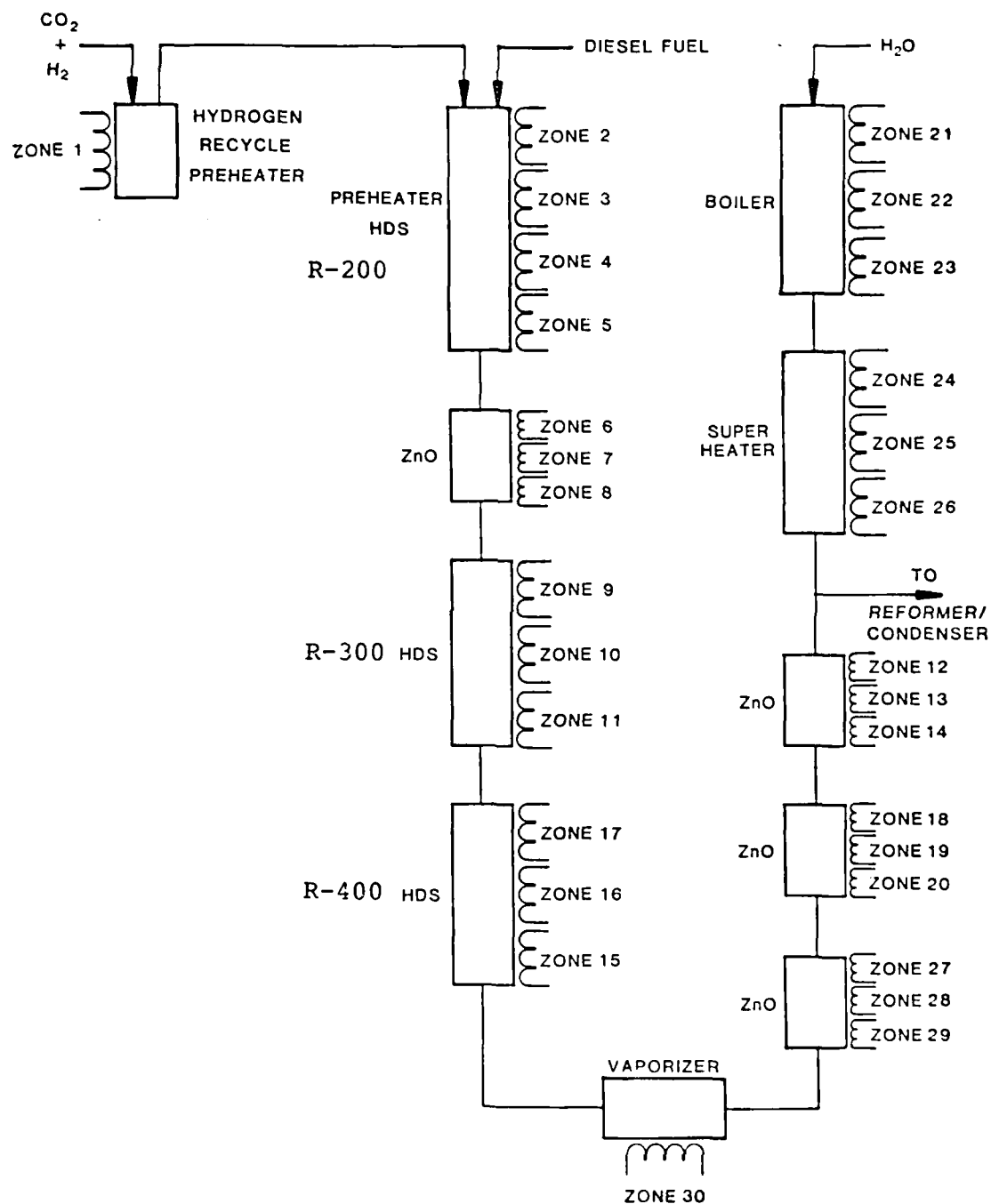
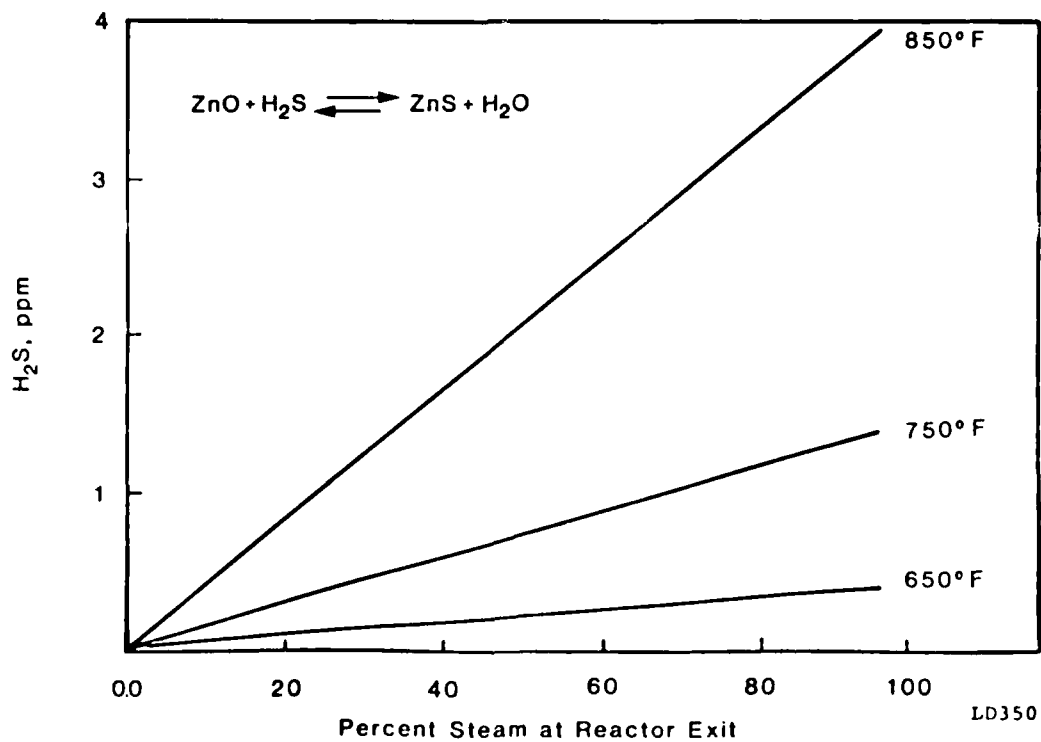


FIGURE 5.1.1  
SULFUR REMOVAL SYSTEM

TABLE 5.1.2  
ZnO REACTOR DESIGN

Number of Identical Units	4
Material of Construction	316 Stainless Steel
Dimensions	2" diam. 18" length
Construction	Sch. 40 pipe
Sorbent Weight (lb.)	2.7 lb ZnO
Temperature	700°F
Pressure	12 psig, 650 psig
Time to Breakthrough at Maximum Sulfur Level (hrs.)	76

FIGURE 5.1.2  
EQUILIBRIUM CONCENTRATIONS FOR THE ZINC OXIDE SYSTEM

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every week during the process demonstration. Regeneration tests were conducted separately as described in Section 6.2.2.

### 5.2 REFORMER

The reformer incorporates an annular catalyst bed and an upfired gas burner. The key design parameters for the reformer are summarized in Table 5.2.

Reformer geometry is shown in Figure 5.2A. The upfired gas burner operates with simulated anode exhaust and compressed air. The burner is shown in Figure 5.2B. It is a vortex burner, with a ceramic lined mixer between the reformer and the combustor. This provides for completion of combustion and insulates the metal from the high temperatures in the burner. Regenerative heat transfer is obtained by passing the product gas on the outside of the catalyst bed before exiting the reformer.

The upper portion of the reformer includes a bellows section in the combustion tube and the outer catalyst wall. This allows for expansion of the metal walls at the high operating temperatures. Figure 5.2C shows the reformer during the 400 hour test.

### 5.3 SHIFT REACTOR

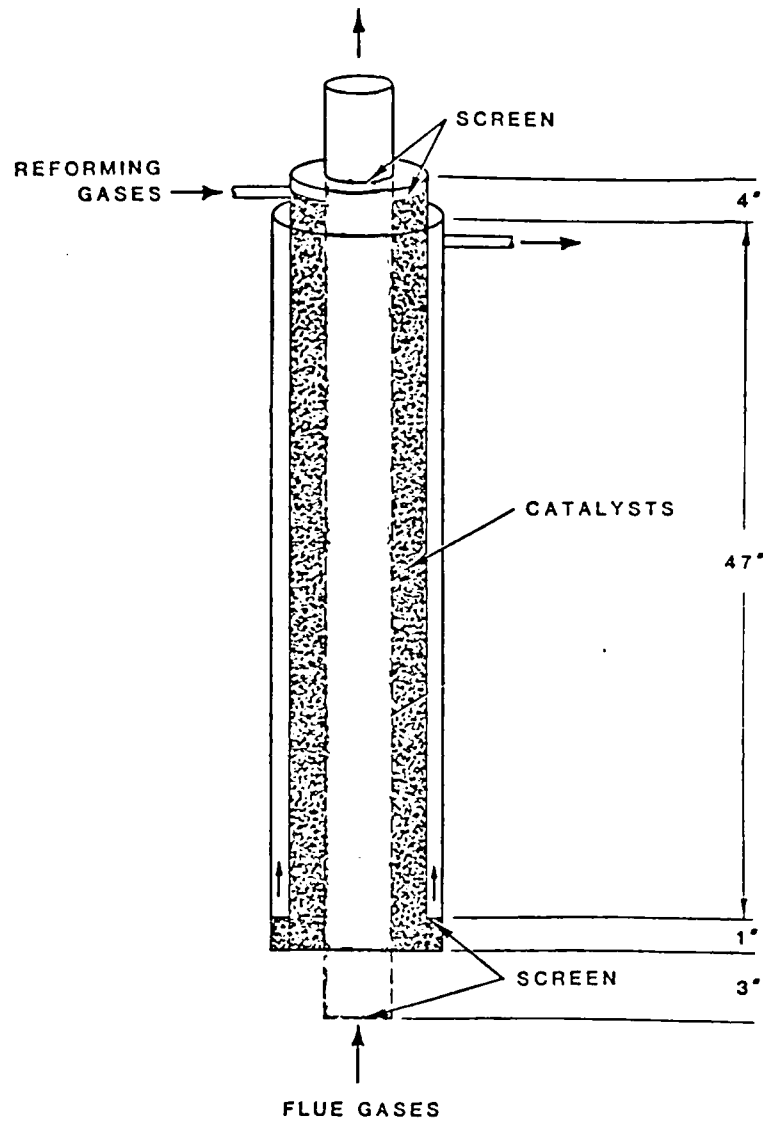
The shift reactors are designed to reduce CO content of the reformer product gas to below 1%. The reactor is a packed bed column. The key parameters for the shift reactors are summarized in Table 5.3. The shift reactors were designed to allow heat dissipation from the reactor walls since small diameter tubes were used. Minimum insulation was used along the length of the reactors, and no insulation was used at the inlet of the first reactor. Figure 5.2C depicts the shift reactors located behind the reformer.

TABLE 5.2  
REFORMER DESIGN

Material:	316 Stainless Steel
Catalyst:	RKNR
Catalyst Volume:	.125 ft <sup>3</sup>
Bed Dimensions, in.:	Annulus between 2.0" O.D. and 3.2" I.D., Height 48"
Space Velocity, STP Product:	5922
Space Velocity as C <sub>1</sub> :	250
Temperature, °F	
Feed Gas:	950
Product Gas:	1300
Burner:	2072
Burner Flue Gas:	1286
Heat Transfer Area, ft <sup>2</sup> :	
Combustion Gas:	1.95
Regenerative Gas:	3.4
Heat Load, BTU/hr:	5259



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Dimensions not  
in proportion.

— Dimensions, in. —			
Tube	Type	OD	Wall Thickness
Inner	SS316	2.0	0.065
Middle	SS316	3.25	0.065
Outer	SS316	4.25	0.237

FIGURE 5.2A  
REFORMER GEOMETRY

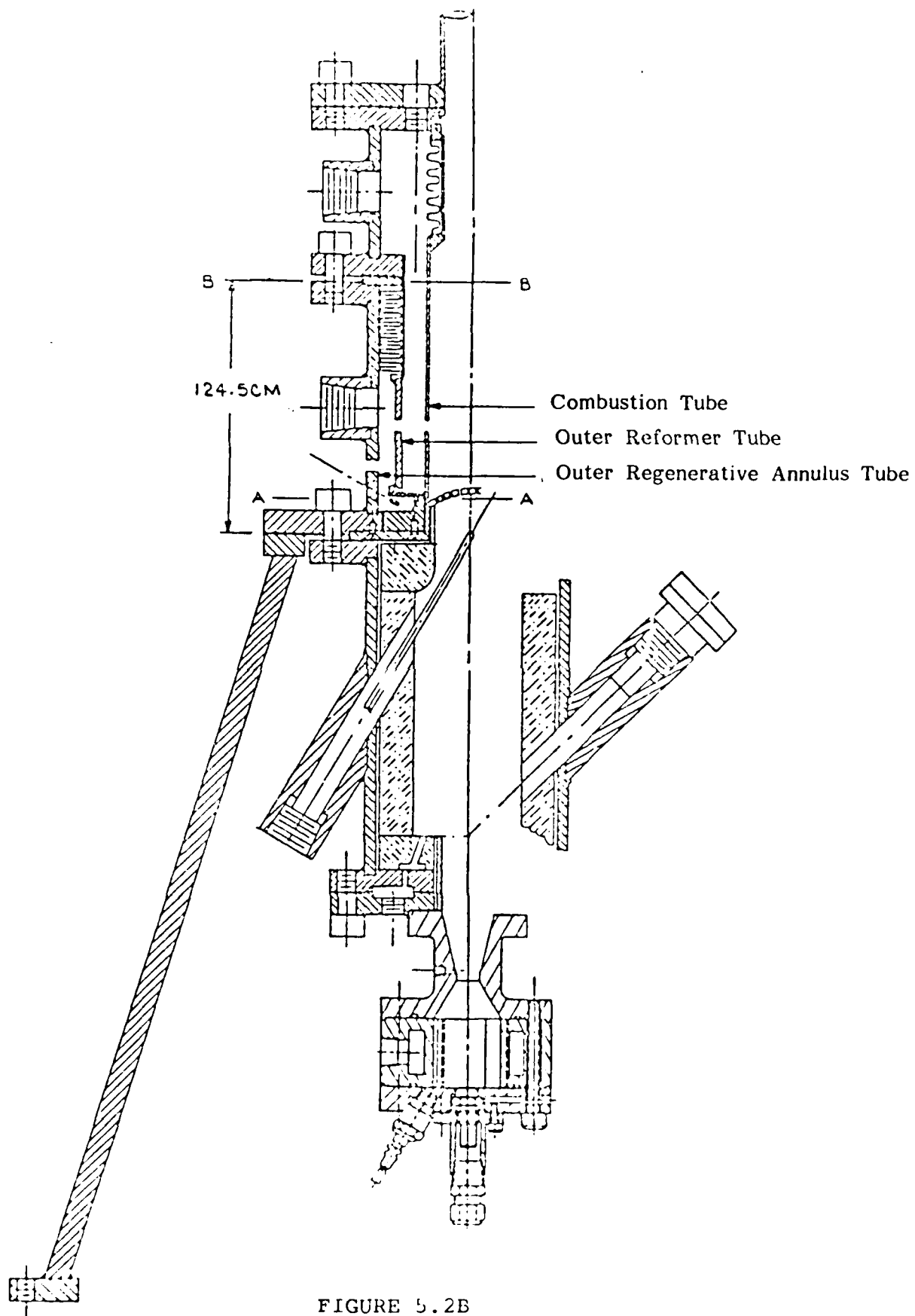


FIGURE 5.2B  
REFORMER BURNER

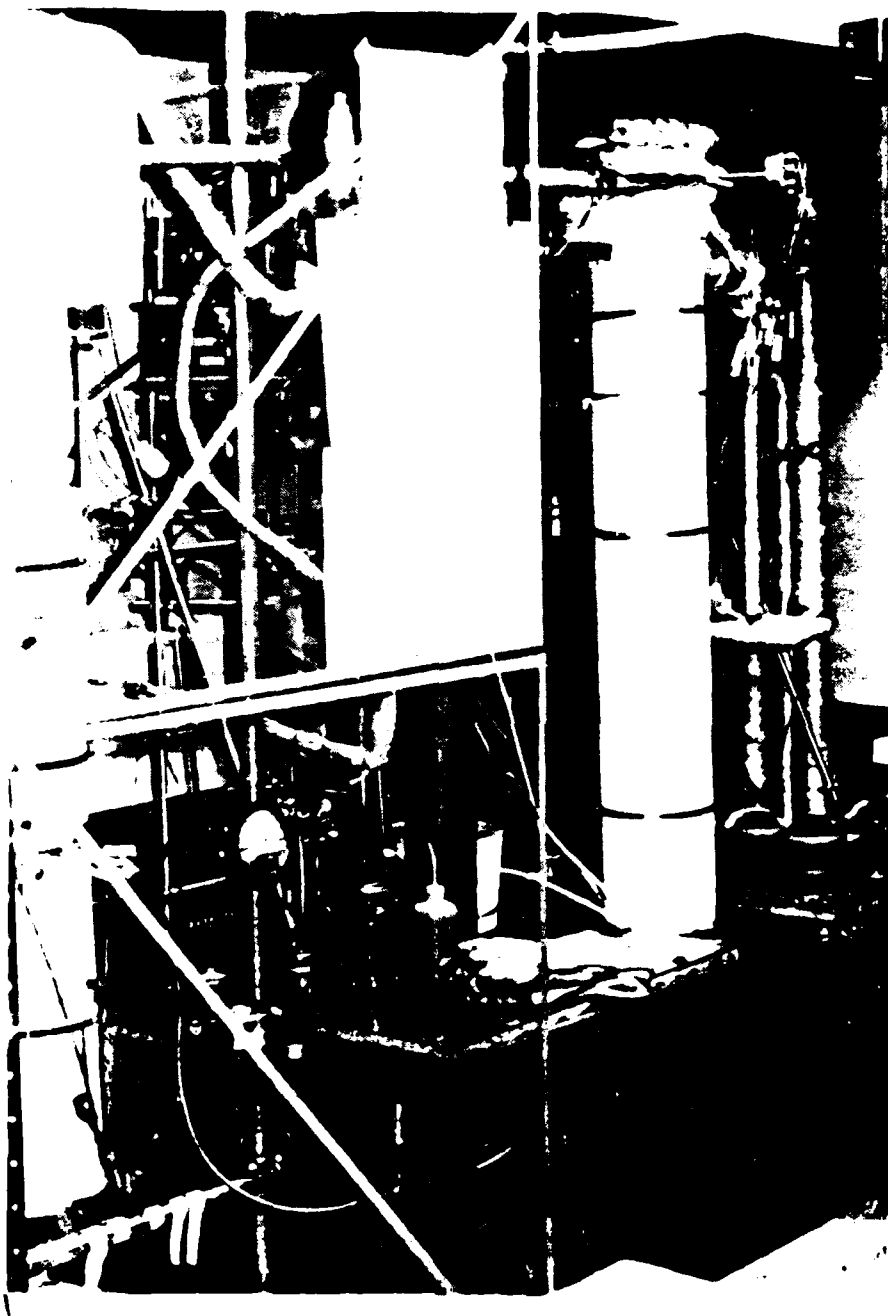


FIGURE 5.2C  
REFORMER AND SHIFT REACTORS DURING 400 HOUR TEST

TABLE 5.3  
SHIFT REACTOR DESIGN

Material:	316 Stainless Steel
Dimensions, in.:	2" dia. 5' length
No. of Reactors:	2
Catalyst:	LK 801
Catalyst Volume:	.20 ft <sup>3</sup>
Space Velocity, STP Product:	924
Space Velocity (dry basis) STP Inlet	550
Temperature, °F	
Inlet:	400
Outlet:	400
Pressure:	1 atm.
Heat Load, BTU/hr.	1812
Heat Transfer Area, ft <sup>2</sup> :	5.2 ft <sup>2</sup>
Heat Transfer Coefficient:	1.06 BTU/hr ft <sup>2</sup> , °F

## 6.0 TEST DATA

### 6.1 SULFUR REMOVAL

Prior to initiating the 400 hour process demonstration test, several tests were conducted with the sulfur removal system at ERC. In addition, prior to and during the process demonstration test, diesel fuel was desulfurized at Haldor Topsoe (at different conditions) in order to provide HDS performance data, and to generate desulfurized fuel for reforming tests required to determine carbon deposition boundaries. Test results from both of these series of tests provide data on desulfurization of diesel fuel at the following conditions:

- PRESSURES            0 psig, 45 psig, 100 psig, 650 psig, 279 psig, 500 psig, 720 psig, 1455 psig
- TEMPERATURE        370-375°C
- SPACE VELOCITIES   0.1 - 7.3 vol/vol/h
- CATALYSTS            TK 550 (Co-Mo) TK551 (Ni-Mo)
- RECYCLE H<sub>2</sub>            100% H<sub>2</sub>, 74% H<sub>2</sub> + 26% CO<sub>2</sub>, 53.2% H<sub>2</sub> + 16.5% CO<sub>2</sub> + 30.3% H<sub>2</sub>O
- NUMBER OF STAGES   1-3

The data obtained during these tests is highlighted in Section 6.1.1.

The sulfur removal tests conducted were by one stage and two stage HDS/ZnO systems at high pressure, and three stage HDS/ZnO systems at low pressure, where the zinc oxide was replaced as necessary during the testing period. A separate series of tests was conducted in which a zinc oxide reactor was sulfided and regenerated nine times in order to provide data on multiple sulfidation/regeneration cycles. Results from these tests are summarized in Section 6.1.2.

### 6.1.1 Hydrodesulfurization

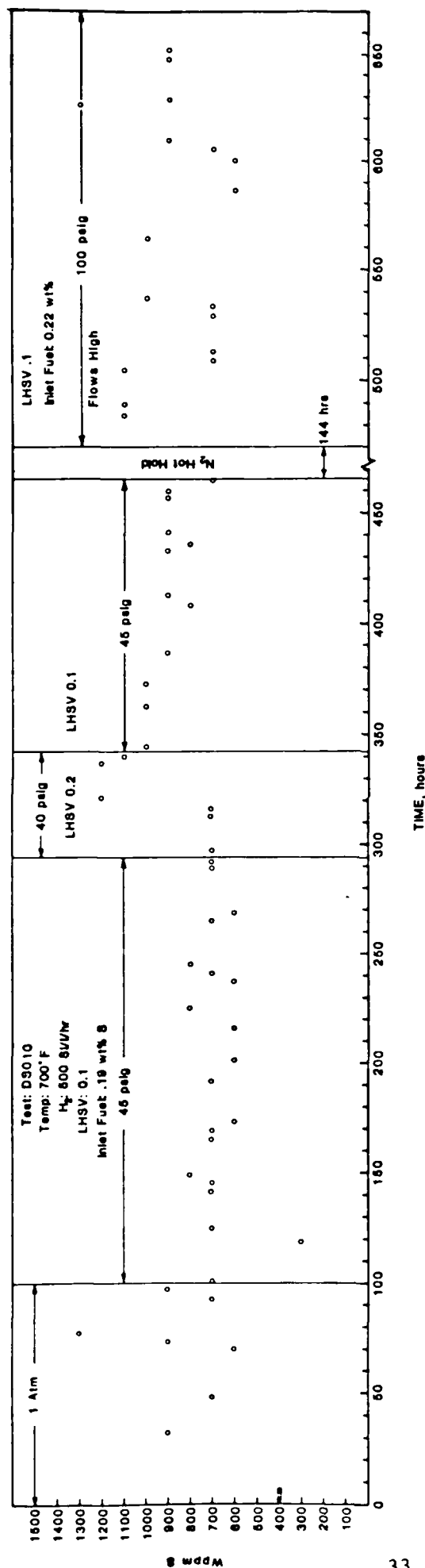
Sulfur removal tests were initially conducted at low pressures (0 psig, 45 psig, and 100 psig). Although initial single stage tests indicated that the desired sulfur removal may be achieved with multiple stages, subsequent testing revealed that hydrodesulfurization of No. 2 Diesel Fuel at low pressures does not achieve the low sulfur level desired in multiple stages with conventional catalysts.

Figure 6.1.1A depicts the sulfur level achieved with a diesel fuel containing 0.19 to 0.22 wt% sulfur. These tests were conducted with a recycle gas containing  $H_2$ ,  $CO_2$  and  $H_2O$ , and with 3 stages of HDS/ZnO. This data indicates that at low pressures the sulfur level was reduced from 0.19 wt% to 700 ppm. The effect of increasing pressure up to 100 psig appeared to reduce data scatter and possibly decay rate, however, it did not achieve the desired sulfur level of less than 1 ppm.

Subsequent tests were conducted at a higher pressure of 650 psig, which is within the range normally used in commercial practice. At the higher operating pressure, the organic sulfur level was reduced to 3-5 ppm in a two stage system. Figure 6.1.1B depicts the data obtained in the first test at pressure. After

was gradually "purged", the organic sulfur level reached a low level of 3-5 ppm in the fuel. In later testing during the process demonstration test, organic sulfur levels below 1 ppm were achieved with two stages of HDS/ZnO.

Testing at Haldor Topsoe was conducted early in the program at pressures of 279 psig, 500 psig, and 720 psig. These tests were conducted with 100%  $H_2$  recycle, and were used to determine the reaction order with respect to sulfur, which was 1.6. In addition, the activity was found to be 1/4 the activity with No. 2 fuel oil. The pressure dependency was determined to be 0.75 in



CATALYST: TK551  
 RECYCLE GAS: 53.2% H<sub>2</sub>, 16.5% CO<sub>2</sub>, 30.3% H<sub>2</sub>O  
 NUMBER OF STAGES: 3

FIGURE 6.1.1A  
 TEST DS010 EXIT SULFUR  
 (ERC Test Data)

SD0331R

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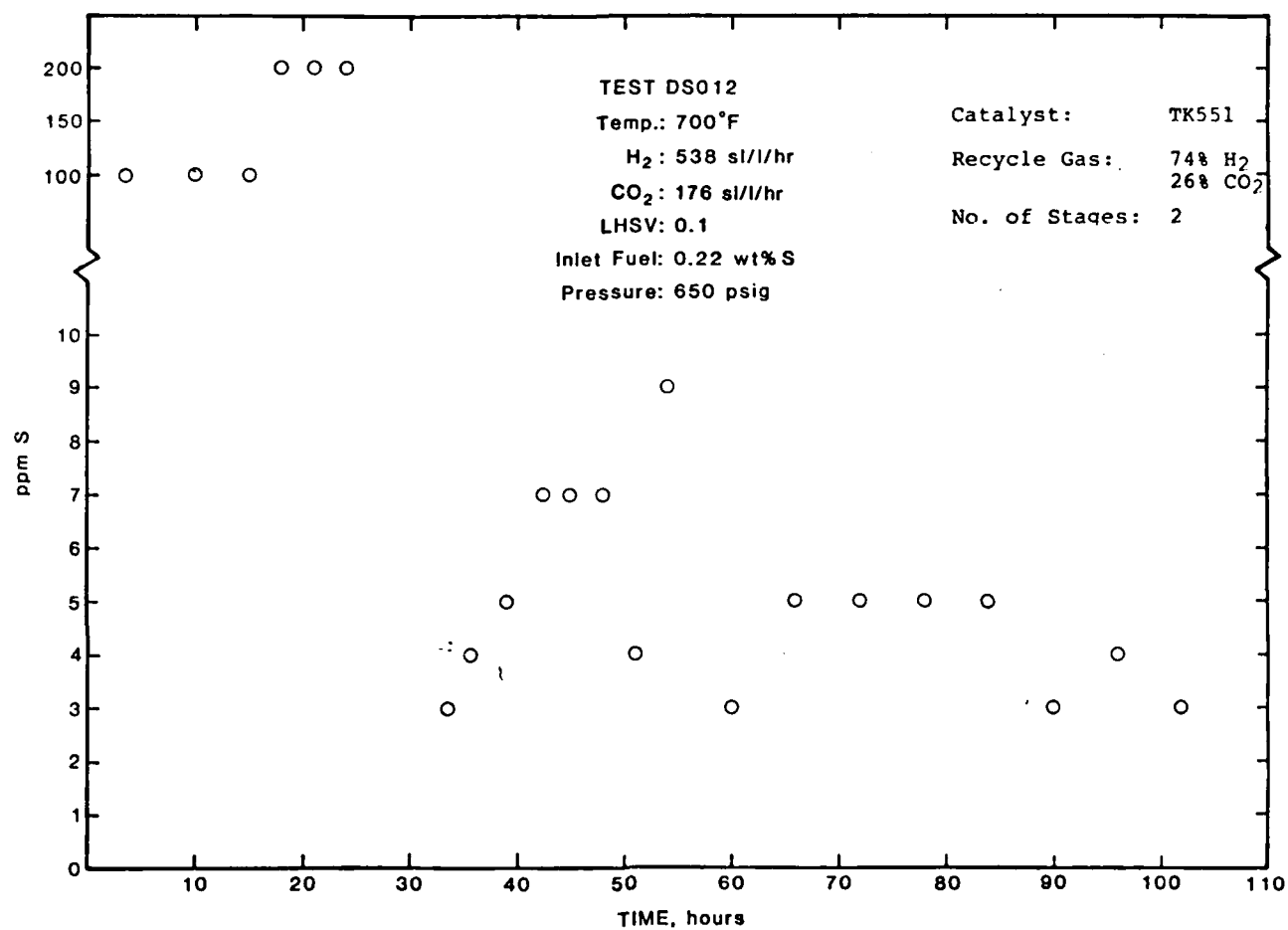


FIGURE 6.1.1B  
 TEST DS012 EXIT SULFUR  
 (ERC TEST DATA)

SD0355



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the range of 279-720 psig. Figure 6.1.1C depicts the data obtained and Figure 6.1.1D depicts the P&I for the test facility at Topsoe. These results, along with test results at ERC indicated that operation at or near 1 atm pressure would not be feasible, and that substantially higher pressures are required. For this reason, the HDS portion of the 400 hour demonstration test was operated at 650 psig pressure.

Longer term operating data was obtained at Topsoe during the preparation of desulfurized fuel for reforming. A total of 1132 hours was accumulated on one batch of catalyst, with organic sulfur being lowered to about 0.4 ppm at the end of the test. A second batch of catalyst accumulated a total of 1268 hours with organic sulfur being lowered to about 0.1 ppm. Figure 6.1.1E depicts the data obtained during these tests. The continuing decline in the sulfur level throughout the test period indicates that contamination from the test equipment continues to be noticeable for many hours, in spite of the fact that the entire system is made of high grade stainless steel with very smooth surfaces. In a larger desulfurizer with higher capacity, the problem with contamination will decrease since the surface/volume ratio of the equipment decreases with increasing capacity.

During the 400 hour process demonstration, the initial sulfur removal was not as good as expected. Figure 6.1.1F depicts the data obtained. The data indicates that prior to the start of the 400 hour test, the HDS subsystem lowered sulfur to 3-5 ppm. Immediately after the start of the 400 hour test, exit sulfur increased to 10-50 ppm. During this period the system was cycled daily and CO<sub>2</sub> purge was used during startup and shutdown. In addition, it was later learned that the purge at each daily shut down was not long enough to purge out the whole system, and therefore some fuel remained in the system. This apparently resulted in either contamination of fuel in the next startup and/or decay of the catalyst. The HDS was operated continuously for nearly 100 hours in order to determine if cycling was the

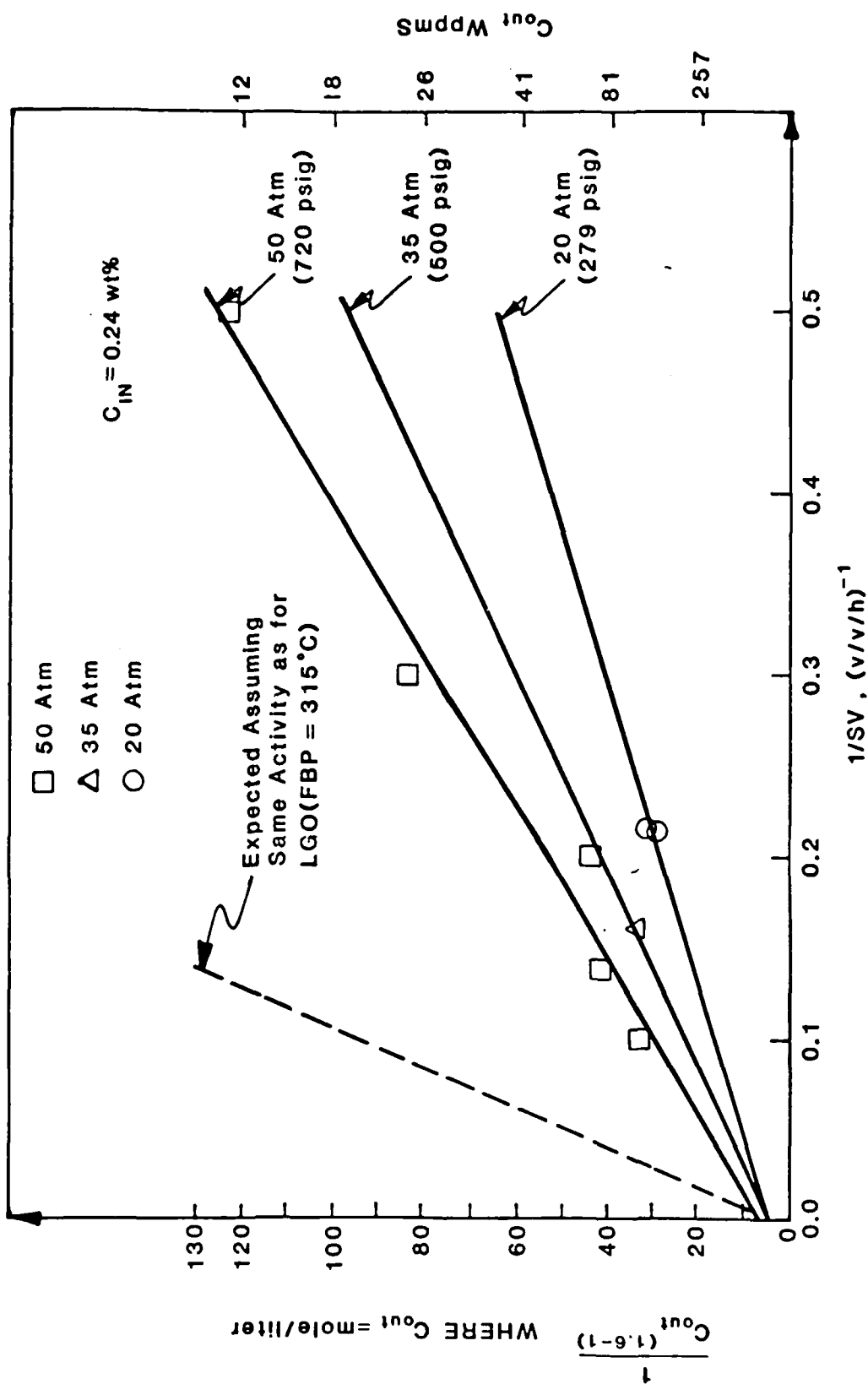


FIGURE 6.1.1C  
EFFECT OF PRESSURE ON HDS ACTIVITY OF FIRST STAGE  
(Topsoe Data)

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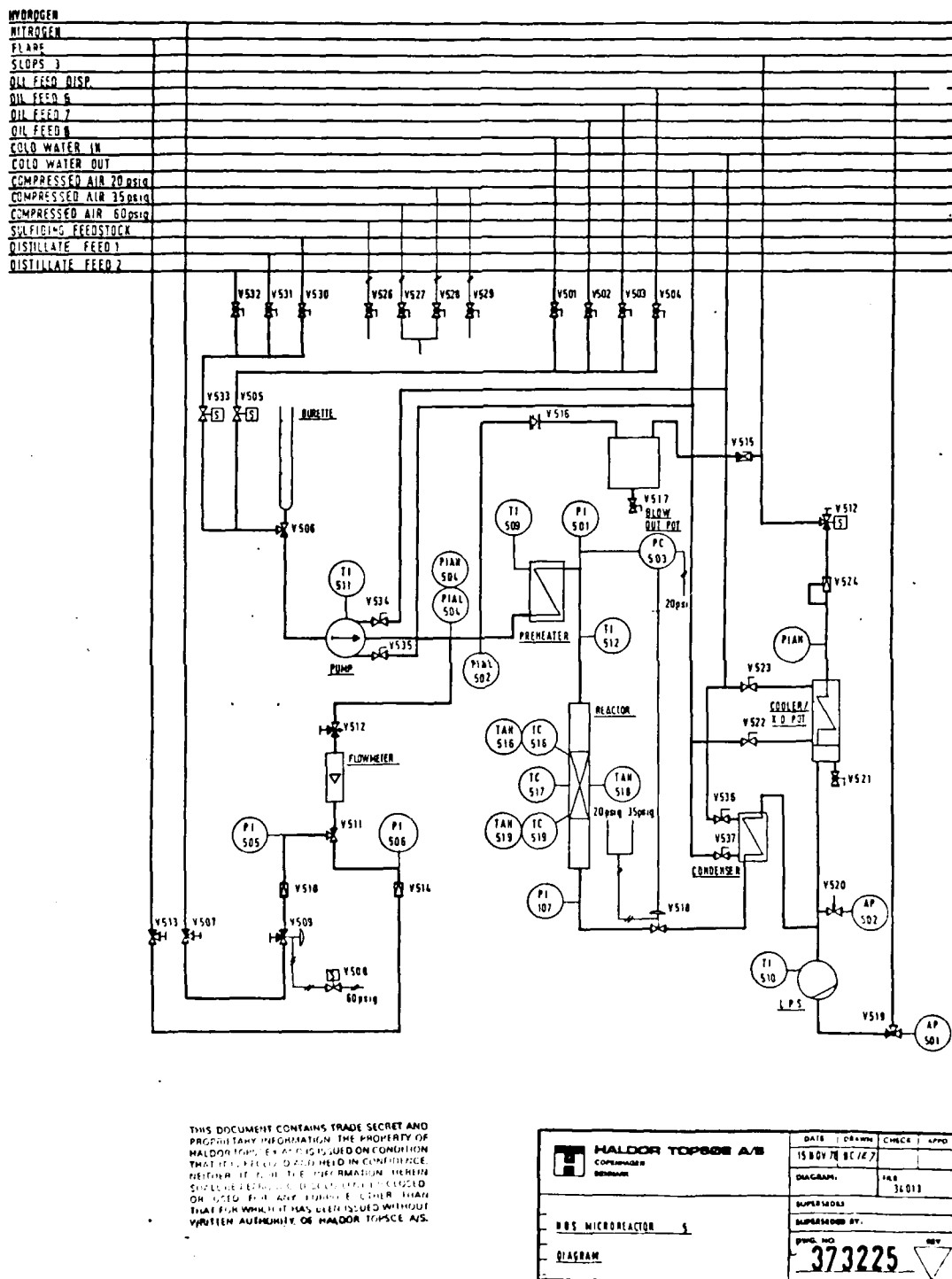


FIGURE 6.1.1D  
TOPSOE HDS TEST FACILITY P&I DIAGRAM

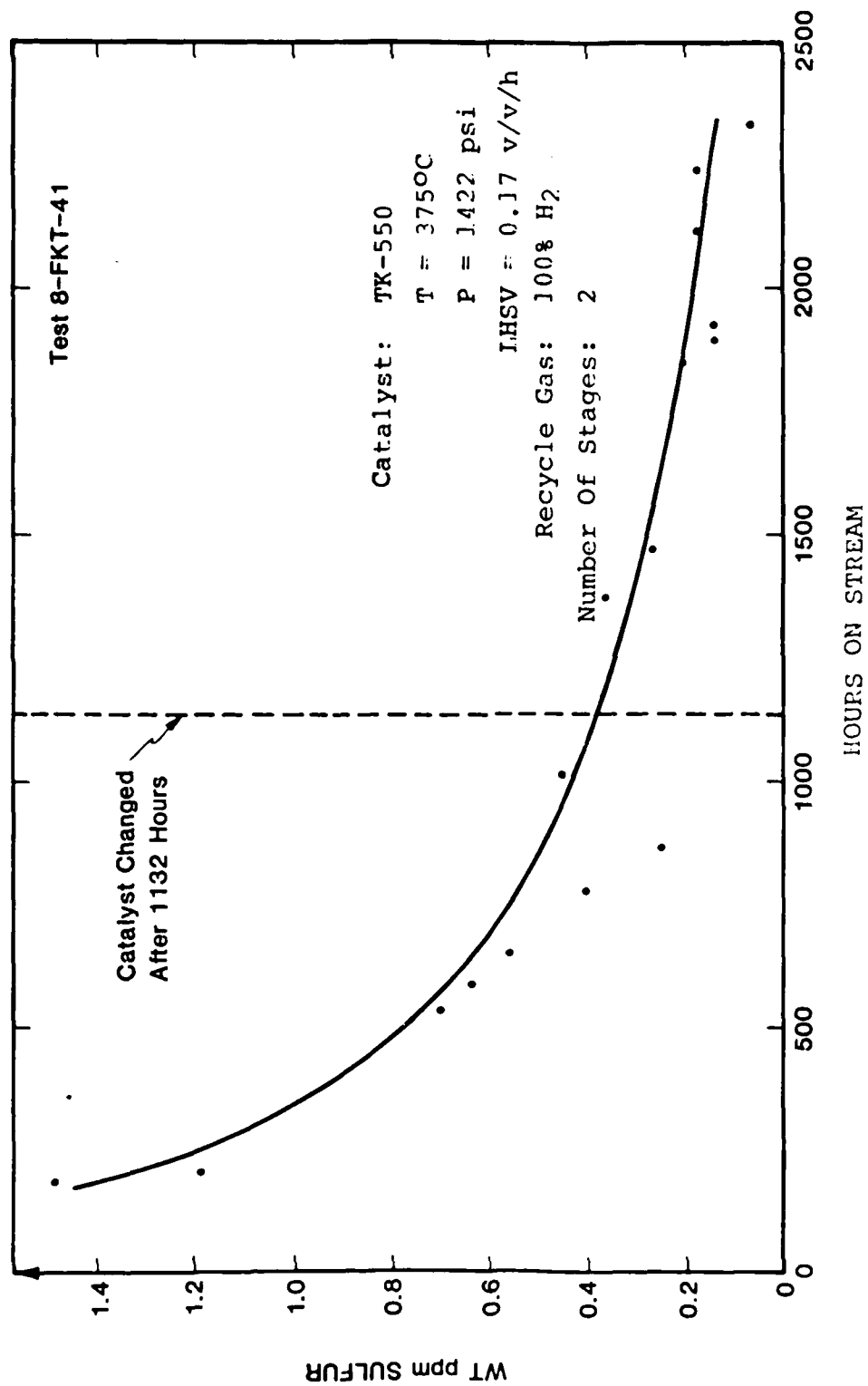


FIGURE 6.1.1E  
SULFUR LEVEL IN DIESEL AS A FUNCTION OF THE HOURS ON STREAM  
(Topsoe Test Data)

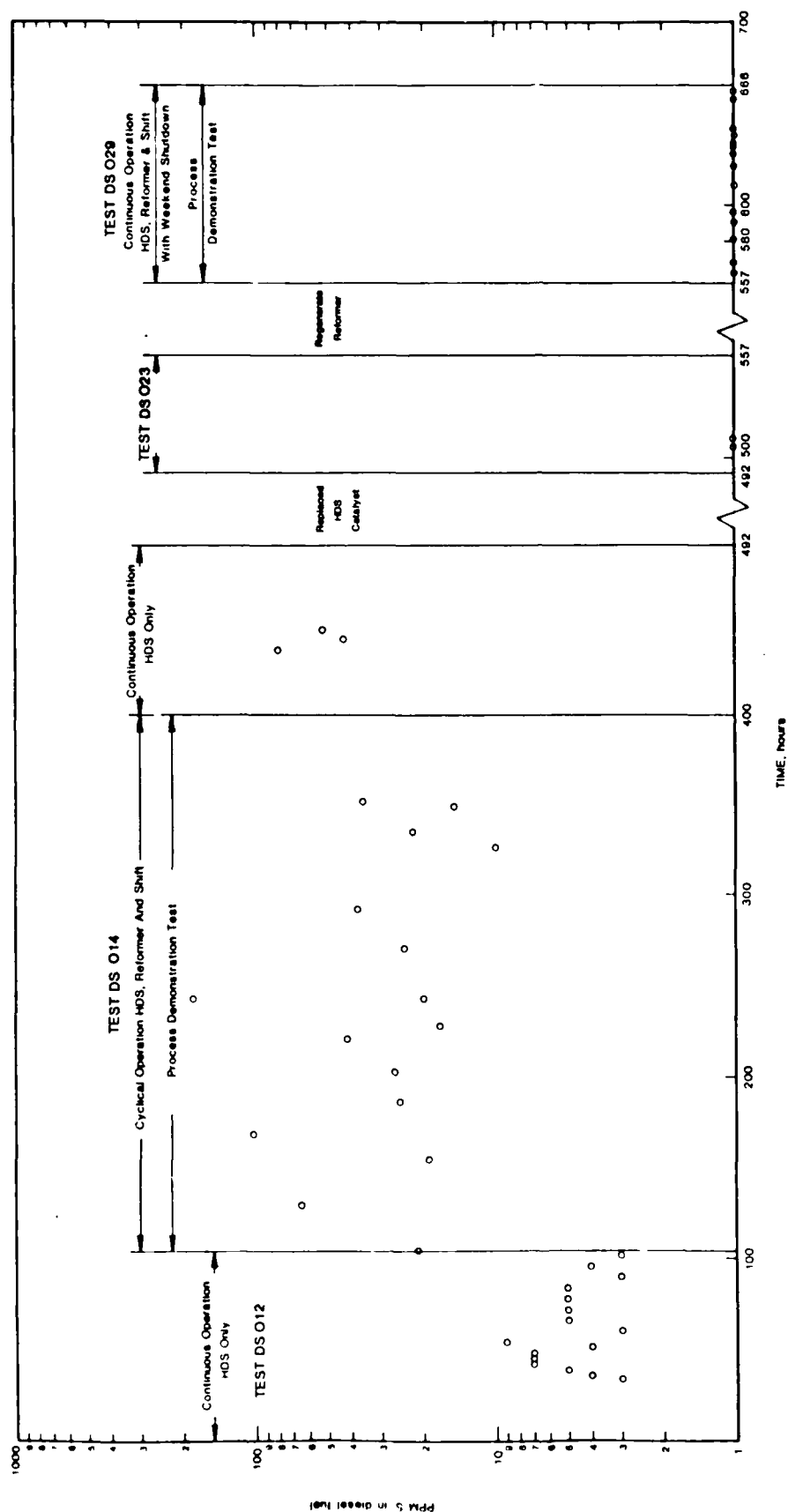


FIGURE 6.1.1F  
SULFUR AT HDS SYSTEM EXIT

NOTES:

1. HDS presulfide conditions: 3% H<sub>2</sub>S (0.552 SL/min) in N<sub>2</sub> at 400-600°F and atmospheric pressure.
2. Operating pressure of HDS: 650 psig.
3. Flow rates: 8.74 gm/min diesel fuel, 5.17 SL/min H<sub>2</sub>, 1.82 SL/min CO<sub>2</sub>.
4. Temperature: 370°C (700°F)

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problem, but no improvement was obtained. Subsequent analysis of the catalyst revealed significant decay with high carbon levels on the catalyst and some loss of sulfiding, particularly at the inlet. Table 6.1 shows the results of the analysis obtained. The expected sulfur content of fully sulfided TK 551 would be between 6.5 and 7.5 wt% on a fresh catalyst. None of the analyzed samples have sulfur content in this range. The sample from the top of Reactor 200 is virtually unsulfided. The carbon levels are also much higher than expected. A reasonable level would be 1-2 wt% carbon.

TABLE 6.1  
ANALYSIS OF HDS CATALYST AFTER 492 TOTAL HOURS OF  
OPERATION  
(298 Hours in the Process Demonstration)

SAMPLE	%C	%S
HDS R-200 Top	12.9	0.40
HDS R-200 Mid	13.3	5.5
HDS R-200 Bottom	11.4	5.5
HDS R-300 Top	12.1	4.1
HDS R-300 Mid	10.2	4.5
HDS R-300 Bottom	11.8	4.5
HDS R-400 Top	12.4	4.5
HDS R-400 Mid	11.3	4.4
HDS R-400 Bottom	11.5	4.1

Although we do not have conclusive evidence as to the reason for these results, Topsoe's experience in distillate service indicates that incomplete sulfiding leads to higher carbon content, and there is a roughly inverse relationship between carbon level and sulfur content. In addition, catalyst activity decreases with decreasing sulfur on the catalyst. Based on the limited amount of testing conducted to date, we attribute the reduced sulfur level on the catalyst (and therefore the higher carbon content) to sulfur being stripped off the catalyst by CO<sub>2</sub>. Carbon dioxide was introduced during startup and shutdown, and was also present in the recycle gas which was 74% H<sub>2</sub> and 26% CO<sub>2</sub>. Subsequently, a new charge of catalyst was loaded, the purge gas was changed to N<sub>2</sub>, and operation was continuous, except for weekend shutdowns, and good performance was obtained for the remainder of the test period (108 hours). The organic sulfur level in the fuel was <1 ppm during this portion of the test. Post test analysis of the catalyst from this portion of the test is discussed on page 72.

#### 6.1.2 Regenerable Zinc Oxide

Multiple sulfidation/regeneration tests were conducted with one zinc oxide reactor identical to the size of the reactors used in the process demonstration test. Accelerated tests were conducted at 10 kW rated flows in which the reactor would be sulfided in H<sub>2</sub>S doped gas typical of HDS effluent, assuming all the sulfur in the fuel is converted to H<sub>2</sub>S. These accelerated flows were used in order to minimize the time to breakthrough. After each breakthrough a regeneration was conducted, and the sulfiding was repeated. Figure 6.1.2A shows the test facility used with a zinc oxide reactor mounted for testing. The zinc oxide reactor is in the center with gas preheaters behind and on each side of the ZnO reactor.

Figure 6.1.2B depicts breakthrough curves for nine sulfidations conducted with regenerations carried out after each

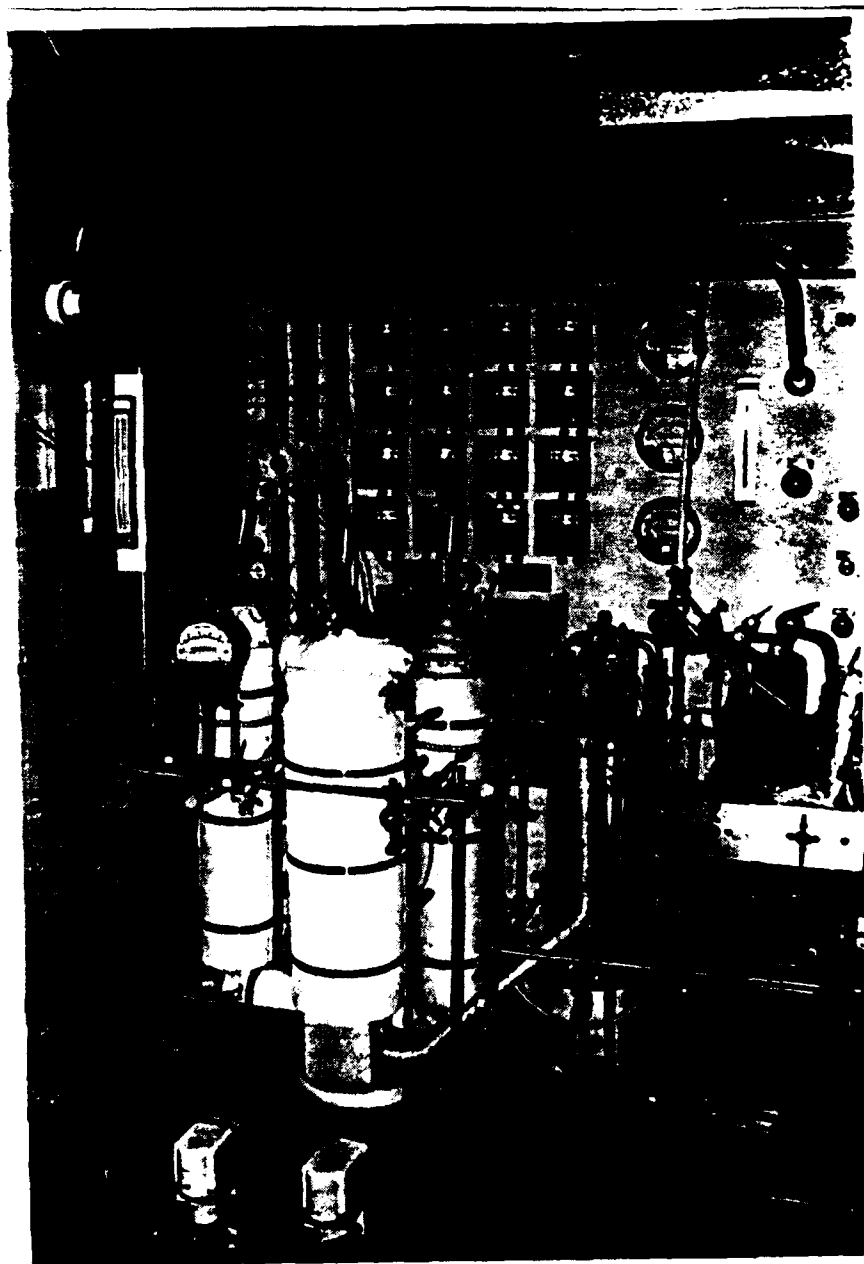


FIGURE 6.1.2A  
ZINC OXIDE SULFIDATION REGENERATION TEST STAND



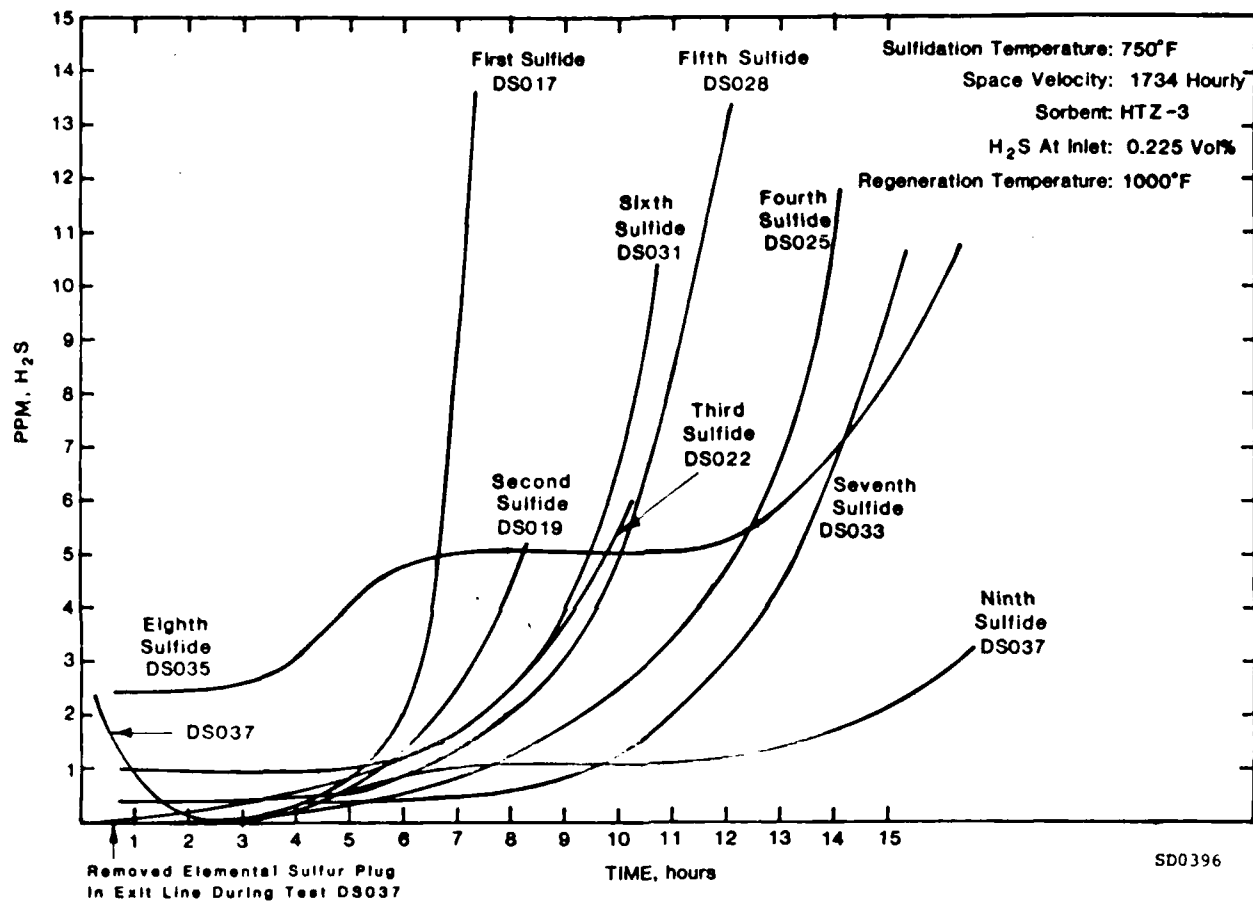


FIGURE 6.1.2B  
MULTIPLE SULFIDATIONS OF ONE ZINC OXIDE REACTOR

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sulfiding, except the last one. The data indicate that the time to breakthrough, and therefore the sulfur loading, actually increased with subsequent regenerations. The breakthrough curves are identified by test number which increase with each successive test, allowing for regeneration tests between sulfidings and other reforming tests. During the eighth sulfiding (Test DS035), higher levels of  $H_2S$  were observed initially and throughout the test. This was later attributed to elemental sulfur which was produced during each regeneration, and had accumulated and condensed in the exit line of the test unit. When this elemental sulfur was removed, the breakthrough curve resumed its normal level. This was done at the beginning of the ninth sulfidation, where it can be seen that the sulfur level started out high, and dropped after the elemental sulfur was removed.

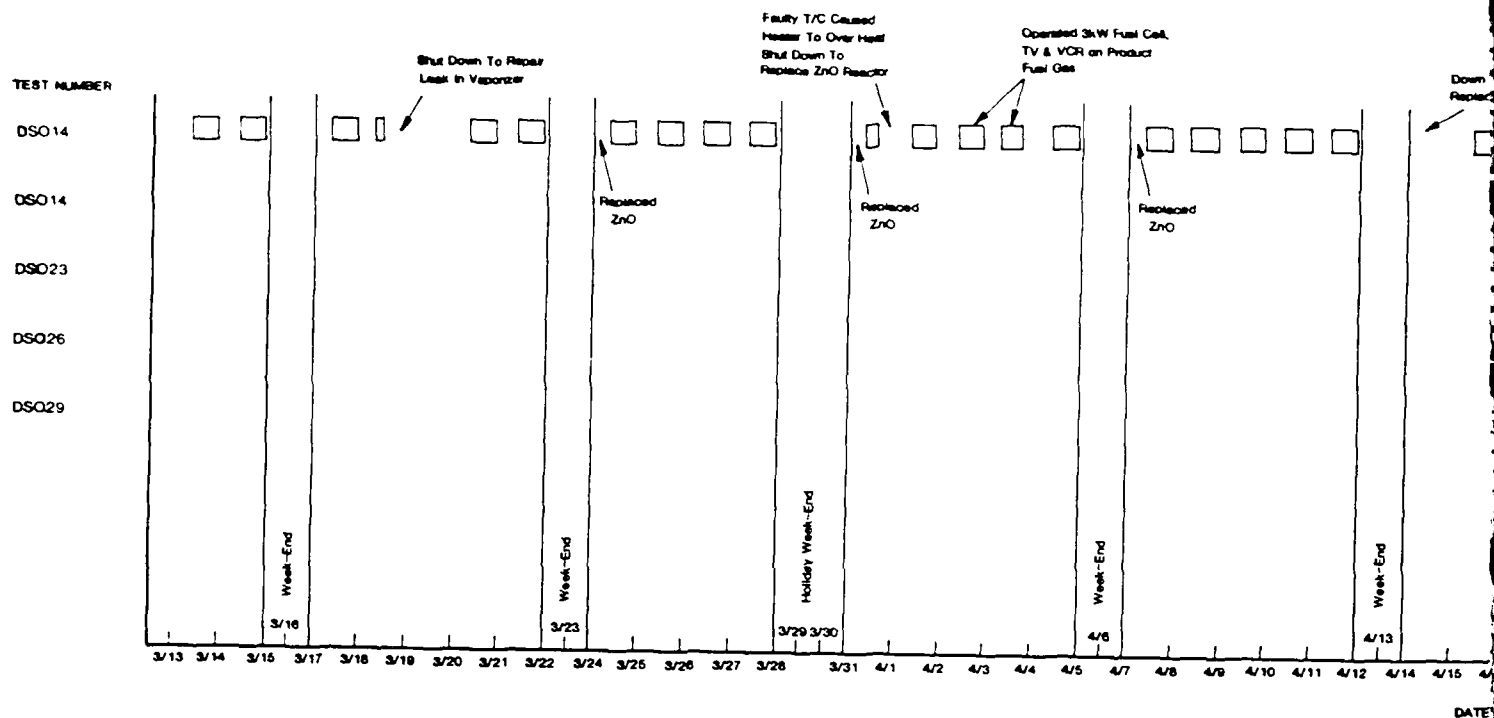
Regenerations were conducted with a 50/50 mol % mixture of steam and air and were usually ended after about 14 hours, at which point the  $SO_2$  level reached about 400 ppm at the exit. Generally, the longer the regeneration is carried out, the lower the  $SO_2$  level will be at the exit, and therefore more of the sulfur is removed from the reactor. At the test conditions used, it was found that upon resuming sulfidation after a regeneration,  $SO_2$  was detected in the exit of the zinc oxide reactor at a level of about 120 ppm (dry basis) which would drop to about 13 ppm in 45 minutes and continue to decrease to 1 ppm after about 2 hours, where it would stay for the duration of the test. This is attributed to residual sulfates in the sorbent which decompose when exposed to the reducing atmosphere of the sulfiding gas. This was observed in other tests of similar sorbents under DOE funded research. To some extent, the extent of this occurrence depends on the length and temperature of the regeneration cycle. The effects of this phenomena on downstream catalysts must be evaluated, although there is some flexibility to minimize this occurrence by duration and conditions of regeneration.

## 6.2 400-HOUR DEMONSTRATION TEST

6.2.1 Schedule of Events

The schedule of events of the 400 Hour Process Demonstration is depicted in Figure 6.2.1. The first 298 hours of operation were accumulated by daily cycling of the fuel processor. This involved a morning startup of about 2 hours followed by operation over a two shift period, and a nightly shutdown. These periods of 15-16 hours of operation (including startup time) were carried out 23 times with 2 exceptions in which repairs were required, and the test unit was shutdown earlier.

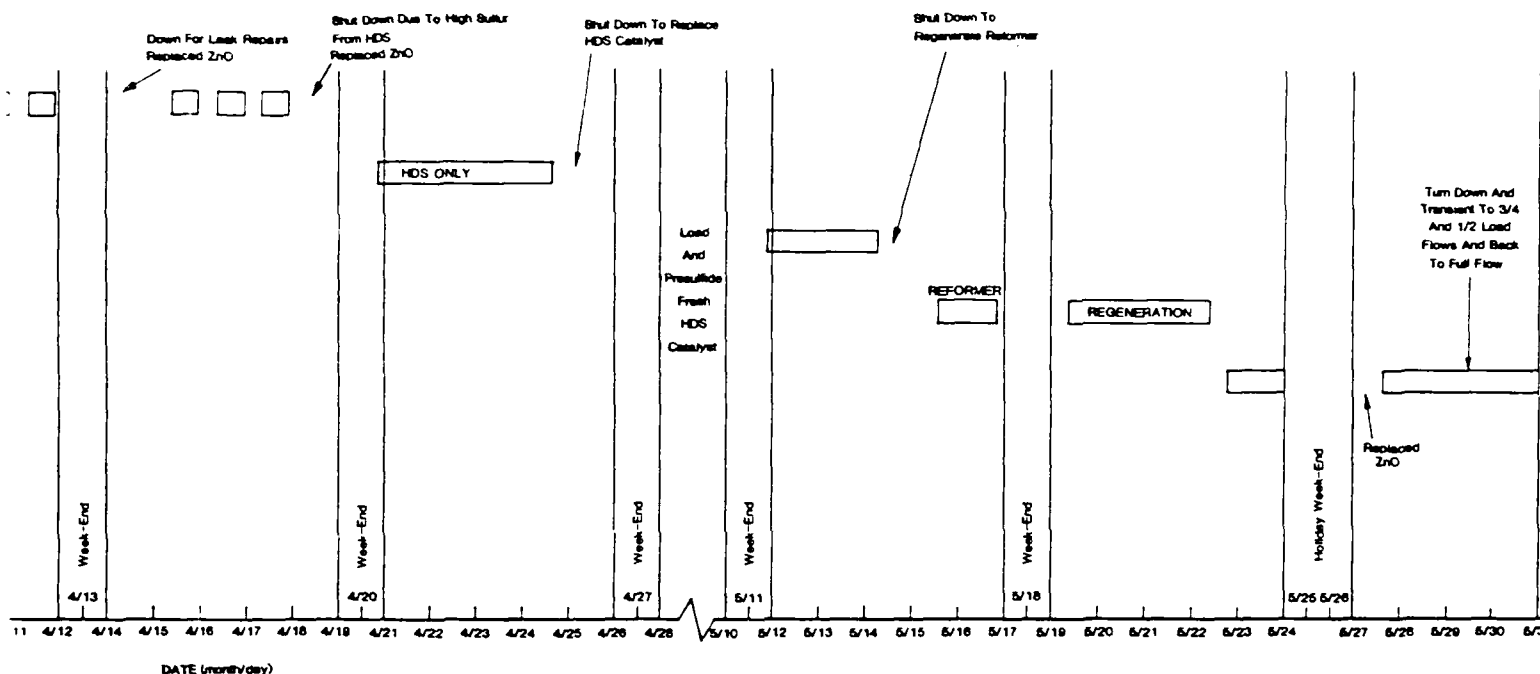
At the 298 hour point, it was evident that the HDS subsystem was allowing high sulfur levels (10-50 ppm) to reach the reformer. At this point the system was shut down and the HDS was operated without the reformer and shift on a continuous basis. This was done because it was suspected that the short term cycling was causing the deterioration in performance or not allowing sufficient time for the system to stabilize. In addition, during a week-end shutdown, a significant amount of diesel fuel was sucked into the HDS system during cool-down, and it was desired to operate for a longer period of time at a steady state condition. When it was determined that continuous operation showed no improvement, the HDS was shutdown and the catalyst removed for analysis. (See Table 6.1, p. 40 and related discussion.) Subsequent analysis revealed the catalyst had decayed. A fresh loading of HDS catalyst was installed, and operated, and when a low sulfur level was verified exiting the HDS, the reformer and shift reactors were brought on stream. At this point, with the reformer inlet being sulfur poisoned during the previous 298 hours of operation, the reformer began to develop a carbon build-up with the low sulfur fuel. The reformer was then shut down and regenerated. This period of testing after the 298 hour mark was not included in the total accumulated test time.



FIGURE

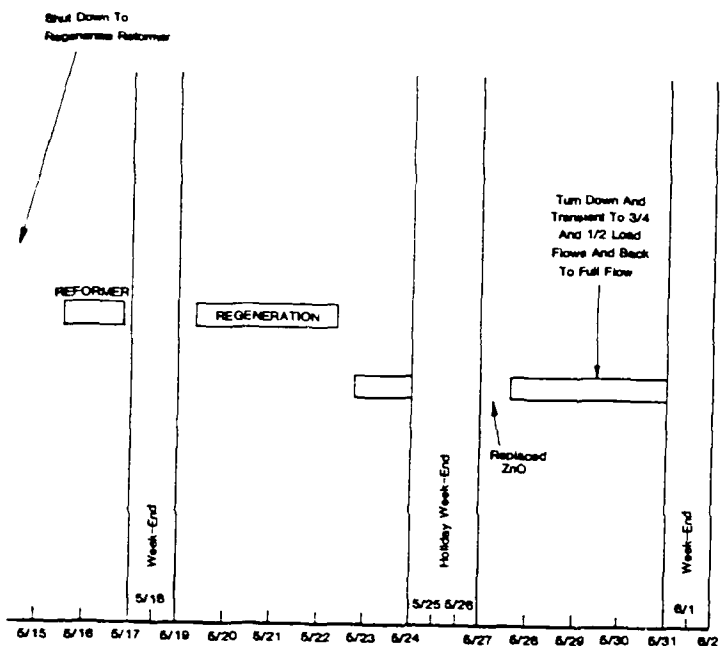
# DIESEL FUEL PROCESS DEMONSTRATION

## SCHEDULE OF EVENTS



500

FIGURE 6.2.1



SD0394

222

After a successful regeneration of the reformer, the remaining 108 hours of operation was conducted continuously with one weekend shut down and a turn down and transient test period which was conducted during one day on the last week of operation. The total accumulated time was therefore 406 hours. Of this total time, 298 hours were accumulated in cyclic operation and 108 hours accumulated in continuous operation. The test period extended from March 13 to May 31, 1986.

#### 6.2.2 400-Hour Process Demonstration Test Data

##### 6.2.2.1 Sulfur Removal

The performance of the sulfur removal subsystem during the 400-hour test, as mentioned in Section 6.1.1, is depicted in Figure 6.1.1D. The 400 hour test period consists of the first 298 hours in which the test unit operated in daily cycles, and the last 108 hours in which the unit was operated continuously after an HDS catalyst change and regeneration of the reformer. The HDS system lowered the sulfur level in the fuel to the 10-50 ppm level in the first portion of the test. This was not as low as desired, and was discussed in Section 6.1.1. After an HDS catalyst change and the change in purge gas and shutdown procedures, a significant improvement was obtained in the HDS performance as shown by the latter part of the curve in Figure 6.1.1D, in which the sulfur level was reduced to below 1 ppm.

The performance of Stage 1 and Stage 2 of the HDS system is further summarized in Table 6.2.2A and Table 6.2.2B. Table 6.2.2B shows the sulfur levels at the second stage HDS exit, both in the fuel and in gas phase (before the ZnO). The average activity for both stages is  $K_{1.6} = 65$  g mole/liter hr.

##### 6.2.2.2 Reformer

The reformer operated at complete conversion of fuel until the high sulfur level leaving the HDS system began to poison the reformer. After approximately 200 hours of operation, traces of

TABLE 6.2.2A  
FIRST STAGE HDS

RUN HOURS	TEMP.		PRESSURE psig	FUEL FLOW gm/min	CO <sub>2</sub> FLOW SL/min	H <sub>2</sub> FLOW SL/min	LHSV
	OC	OF					
49	370	(698)	650	8.74	1.82	5.17	.22
56	370	(698)	650	8.74	1.82	5.17	.22
70	370	(698)	650	8.74	1.82	5.17	.22
76	370	(698)	650	8.74	1.82	5.17	.22
82	370	(698)	650	8.74	1.82	5.17	.22
112	370	(698)	650	8.74	1.82	5.17	.22
125	370	(698)	650	8.74	1.82	5.17	.22
131	370	(698)	650	8.74	1.82	5.17	.22
135	370	(698)	650	8.74	1.82	5.17	.22
139 (Turn Down 3/4 Flow)	370	(698)	650	6.55	1.36	3.87	.16
143 (Turn Down 1/2 Flow)	370	(698)	650	4.37	.91	2.58	.11
149	370	(698)	650	8.74	1.82	5.17	.22
160	370	(698)	650	8.74	1.82	5.17	.22
169	370	(698)	650	8.74	1.82	5.17	.22
173	370	(698)	650	8.74	1.82	5.17	.22

1. Sulfur in Diesel Fuel = 0.28 wt%
2. Data from Test DS023 and DS029
3. Catalyst is TK 551



TABLE 6.2.2B  
SECOND STAGE HDS

RUN HOURS	TEMP.		PRESSURE psig	FUEL FLOW gm/min	CO <sub>2</sub> FLOW SL/min	H <sub>2</sub> FLOW SL/min	Sout ppmw in fuel	Sout ppmw in gas	LHSV
	OC	OF							
15	370	(698)	650	8.74	1.82	5.17	<1	200	.14
18	370	(698)	650	8.74	1.82	5.17	<1	200	.14
72	370	(698)	650	8.74	1.82	5.17	<1	200	.14
77	370	(698)	650	8.74	1.82	5.17	<1	200	.14
90	370	(698)	650	8.74	1.82	5.17	<1	225	.14
101	370	(698)	650	8.74	1.82	5.17	<1	110	.14
106	370	(698)	650	8.74	1.82	5.17	<1	110	.14
121	370	(698)	650	8.74	1.82	5.17	<1	250	.14
131	370	(698)	650	8.74	1.82	5.17	<1	300	.14
138 (Turn Down 3/4 Flow)	370	(698)	650	6.55	1.36	3.87	<1	45	.10
141	370	(698)	650	8.74	1.82	5.17	<1	55	.14
143 (Turn Down 1/2 Flow)	370	(698)	650	4.37	.91	2.58	<1	37	.07
149	370	(698)	650	8.74	1.82	5.17	<1	100	.14
153	370	(698)	650	8.74	1.82	5.17	<1	100	.14
169	370	(698)	650	8.74	1.82	5.17	<1	100	.14
173	370	(698)	650	8.74	1.82	5.17	<1	95	.14

1. Data from Test DS023 and DS029
2. Catalyst is TK 551

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hydrocarbons were detected in the exit gas, and after 268 hours, hydrocarbons were detected in the condensate. Table 6.2.2C summarizes the operating parameters of the reformer.

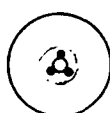
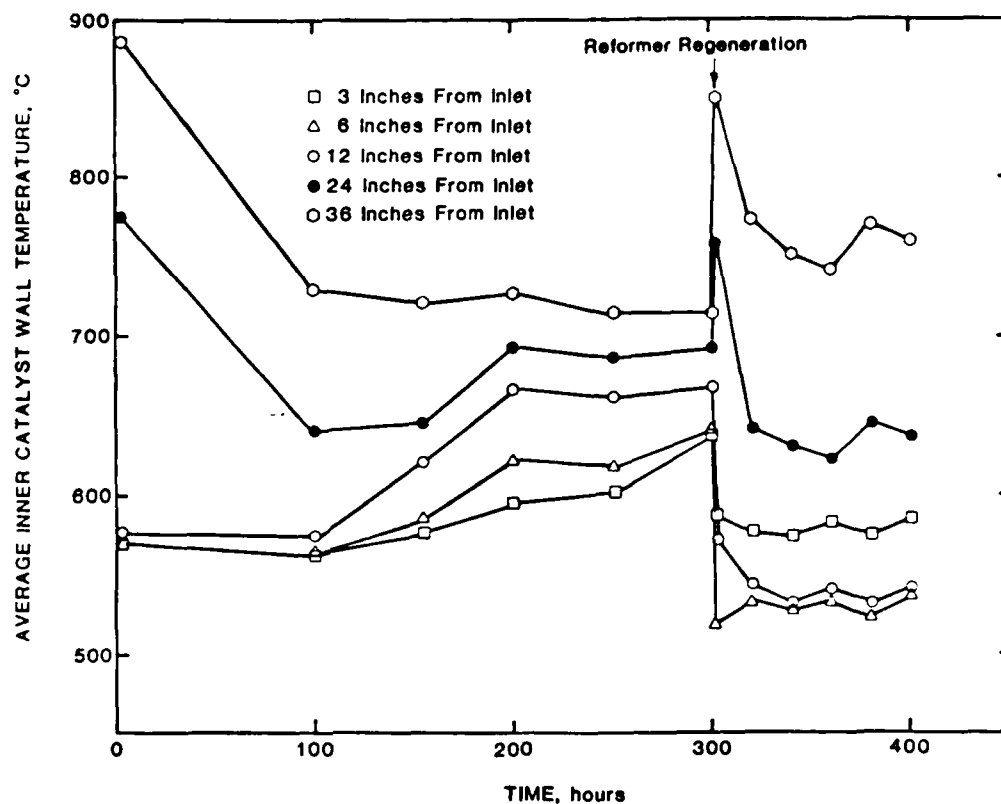
Temperatures in the reformer are summarized in Figure 6.2.2A. The data shows a gradual shifting of the reforming zone from the inlet as sulfur is building up on the reformer catalyst up to the 298 hour mark. After the regeneration of the reformer, the temperature profile of the reformer resumed a sulfur free mode with stable reforming occurring throughout the reformer. The lower temperatures observed near the reformer inlet indicate that more reforming is occurring at the inlet after the 300 hour mark due to the lower sulfur content of the fuel in this portion of the test.

Gas analysis at the reformer exit indicated that gas compositions were close to the expected equilibrium. Table 6.2.2D shows the gas compositions obtained, and the expected equilibrium levels. The methane content was observed to increase slightly during the first 298 hours of testing as the reformer was "sulfur poisoned" by the high levels of sulfur leaving the HDS. After this was corrected, the methane content dropped back down.

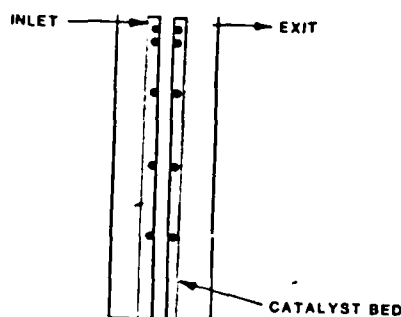
Reformer pressure drop was stable during the first 300 hours of operation at about 1 1/2 psig. After the 300 hour mark, the HDS catalyst was replaced, and HDS performance was improved to <1 ppm sulfur fuel entering the reformer. Operation of the reformer with the low sulfur fuel resulted in rapid carbon build-up within the first nine hours of operation. Figure 6.2.2B depicts the reformer pressure drop during the 400 hour process demonstration. The rapid carbon build-up is attributed to the fact that the reformer had been partially deactivated during the first 300 hours of operation, and the low sulfur fuel entering the reformer resulted in incomplete reforming at the inlet and production of olefins which are precursors of carbon formation.

TABLE 6.2.2C  
DIESEL FUEL PROCESS DEMONSTRATION TEST  
TYPICAL OPERATING PARAMETERS

TOTAL HOURS:	406.5
DIESEL FUEL FLOW (gm/min):	8.7
WATER FLOW (H <sub>2</sub> O/C = 5.5) (gm/min):	62.6
HYDROGEN FLOW TO HDS (SL/min):	5.17
CO <sub>2</sub> FLOW TO HDS (SL/min):	1.82
SULFUR LEVEL AT REFORMER INLET (ppmw in fuel)	10-50 ppm First 300 Hours Less Than 1 ppm Last 100 Hours
REFORMER INLET TEMPERATURE (°F):	950
REFORMER CATALYST BED EXIT TEMPERATURE (°F):	1280
REFORMER PRESSURE DROP (psig):	2.1



TOP VIEW



SIDE VIEW

FIGURE 6.2.2A

REFORMER CATALYST WALL  
TEMPERATURES TEST DS014

NOTE: 1. Temperatures are average of three temperatures 120° apart on the combustion tube wall at the elevation indicated.

TABLE 6.2.2D  
EXIT GAS COMPOSITIONS  
DRY BASIS

## REFORMER EXIT

	MEASURED			EQUILIBRIUM VOL %
	127 HR VOL %	275 HR VOL %	346 HR VOL %	
H <sub>2</sub>	72.29	71.72	71.87	71.5
CO	10.11	8.15	9.92	10.5
CO <sub>2</sub>	17.32	19.50	17.43	17.8
CH <sub>4</sub>	.04	.52	.01	.28

## NOTE:

1. Higher CH<sub>4</sub> content observed when the reformer catalyst was poisoned by sulfur at the 275 hr point.
2. Equilibrium based on 760°C (1400°F) reformer catalyst exit temperature, H<sub>2</sub>O/C = 5.5 at reformer inlet. Recycle gas composition 73.9% H<sub>2</sub>, 25.4% CO<sub>2</sub>, 0.4% H<sub>2</sub>O, 0.2% CO, 59 psig reformer pressure.
3. Actual catalyst bed exit temperature was approximately 693°C (1280°F), exit pressure 10 psig.

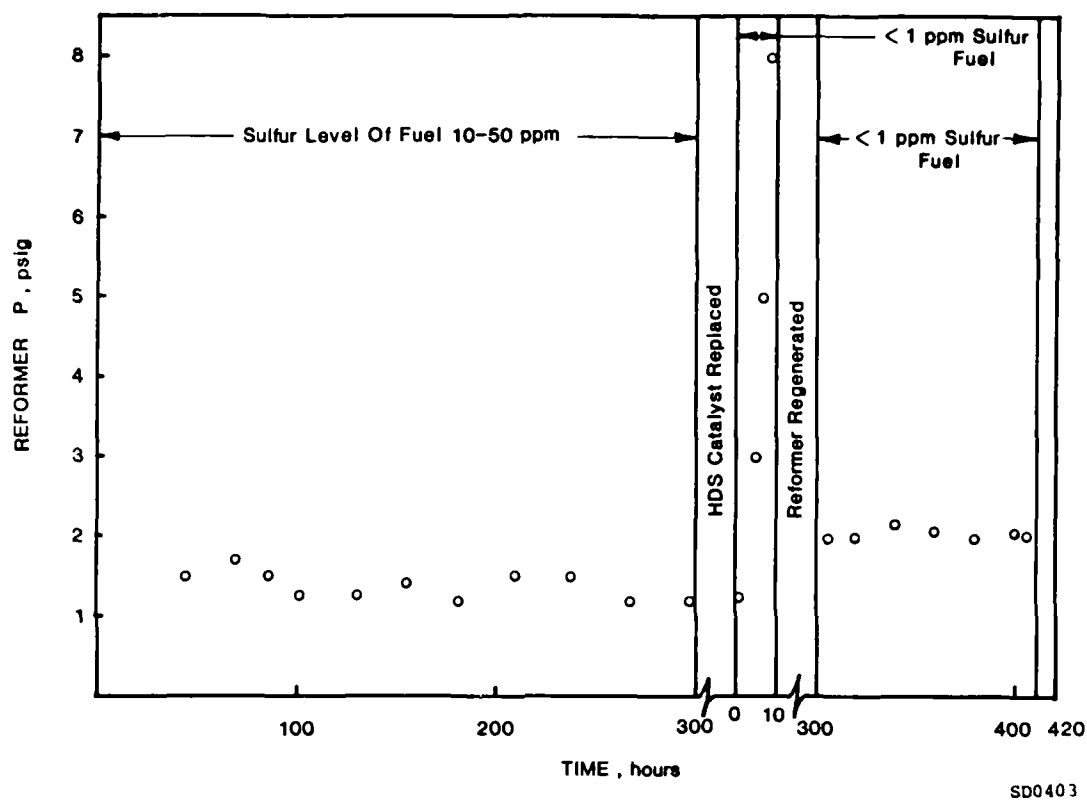


FIGURE 6.2.2B  
REFORMER PRESSURE DROP

The presence of sulfur in the first 300 hours of operation served to inhibit the formation of carbon. This effect was demonstrated with natural gas (see Catalytic Steam Reforming, J.R. Rostrup-Nielsen p. 104) where it was shown that sulfur inhibits the carbon formation more than it inhibits the reforming reaction. When the sulfur was suddenly lowered, a dramatic increase in carbon formation was observed, since sulfur was no longer present to inhibit the formation of carbon. Had the reformer been operating with low sulfur at the inlet from the start, the reformer catalyst would have remained in a highly active state and this carbon buildup would not have occurred.

The reformer was regenerated following the carbon buildup to remove carbon and sulfur. The regeneration conditions are outlined in Table 6.2.2E. Following the regeneration, the pressure drop resumed a value slightly higher than its previous operating point, and stayed at about 2 psig throughout the remainder of the test program.

#### 6.2.2.3 Shift Reactors

The shift reactor operating temperatures are depicted by Figure 6.2.2C. This data shows two typical daily cycles carried out during the 400-Hour Process Demonstration Test. The data indicates an inlet temperature of about 265°C, and a gradual decrease in temperature, due to heat loss to an exit temperature of about 100°C. The exit temperature was lower than desired, but was tolerated in order to keep the test facility simple. The temperature profile obtained was due to heat losses, and no attempt was made to provide electrical heat to maintain temperatures in the shift reactors.

Gas analysis after the shift reactors indicate that good reduction of the CO level was obtained, with 0.1% CO measured earlier in the test and 0.25% CO measured at the end of the test.

TABLE 6.2.2E  
REFORMER REGENERATION CONDITIONS

	CARBON REMOVAL		SULFUR REMOVAL	
	Flow Rate	Vol %	Flow Rate	Vol %
Air	1.39-4.17 scfh	2-8	-	-
Steam	3.3 lb/hr	92-98	3.3 lb/hr	75-98
H <sub>2</sub>	-	-	1.39-23.15 scfh	2-25
CO <sub>2</sub> at Reformer Exit	-	<0.1%	-	-
H <sub>2</sub> S at Reformer Exit	-	-	-	<10ppm
Temperature of	<1112		<1382	
Time Hours	39		57	



TEST #DS014

DATE 04/07/86

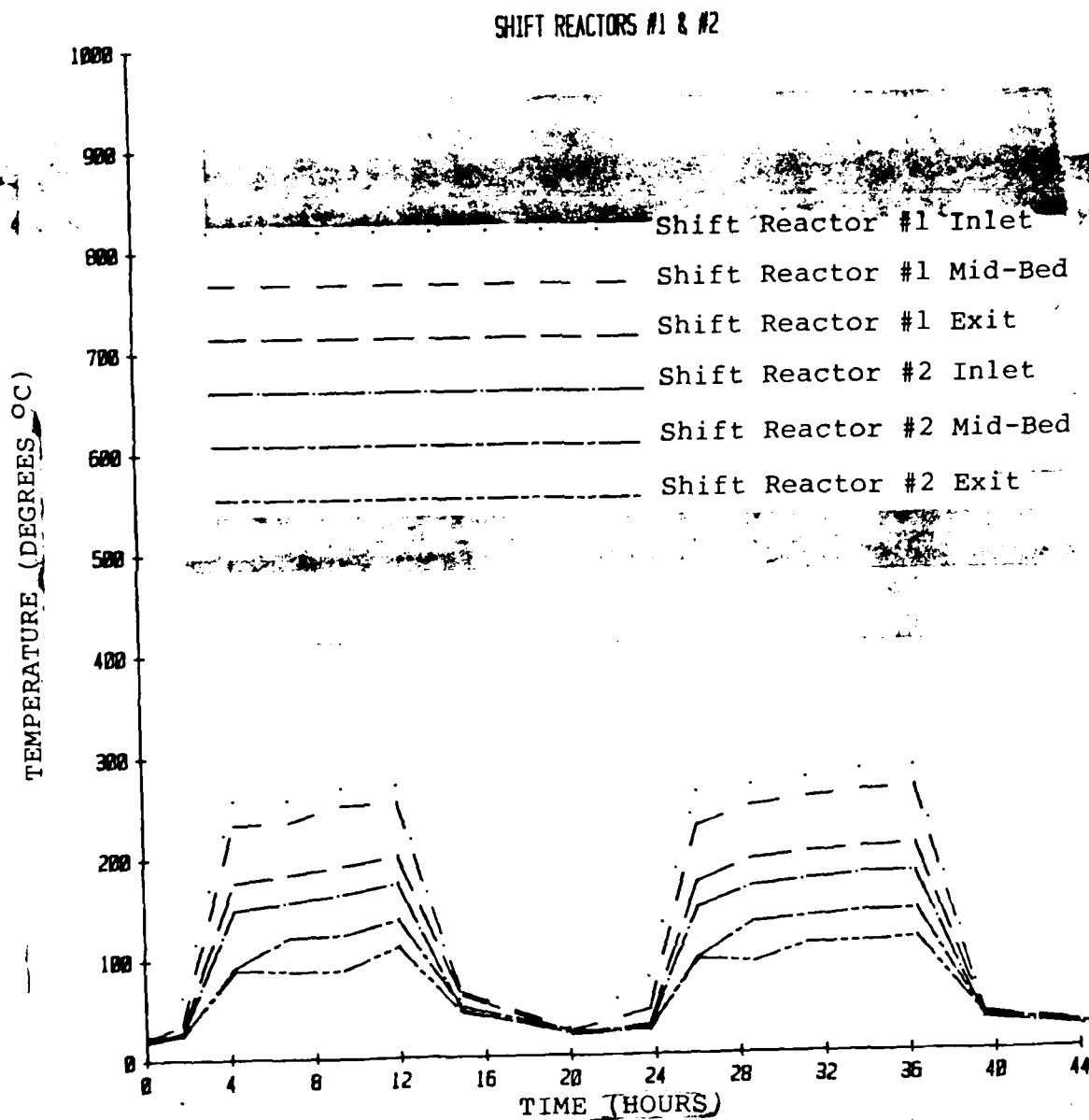


FIGURE 6.2.2C  
DIESEL FUEL PROCESSING  
TEMPERATURE PROFILE  
IN SHIFT REACTORS

Table 6.2.2.3 depicts the gas compositions measured, and the equilibrium expected. The increase in CO level during the test is due to the partial sulfur poisoning of the shift reactor during the first 298 hours of the test.

### 6.2.3 Turn Down and Transients

Turn down and transients were tested by reducing flows to 3/4 flows and back to full flows, followed by reduction to 1/2 flows and back to full flows. These turn downs were accomplished by reducing the flows of fuel and gases at the metering point. Steam flow and gas flows to the reformer burner were not reduced during these turn down tests. It is anticipated that these flows will be maintained or reduced partially in a full scale power plant in order to improve transient response. Parameters monitored during turn down and transients were as follows:

- Temperatures
- Exit Flow
- H<sub>2</sub> Composition
- CO Composition

The data obtained on temperature profiles indicates a negligible effect on overall inlet and outlet temperature for the reformer and shift reactors. Figures 6.2.3A and 6.2.3B illustrate the temperature profiles recorded for the shift reactors and reformer inlet and exit. A look at the internal temperatures in the reformer (Figure 6.2.3C) indicate a more visible effect of transients. It appears that the effects of step changes in flows require about 1-2 hours to stabilize in terms of temperatures on the catalyst walls. This was obtained with no change in burner flows, as mentioned earlier.

Effect of transients on H<sub>2</sub> and CO levels leaving the fuel processor are illustrated in Figures 6.2.3D, 6.2.3E, 6.2.3F, and 6.2.3G. These results were obtained by LIRA (infra red) analysis, (MSA Model 303 for CO and MSA Thermocon Analyzer Model T-3 for H<sub>2</sub>) which

TABLE 6.2.2.3  
EXIT GAS COMPOSITIONS  
DRY BASIS

## SHIFT EXIT

	MEASURED				EQUILIBRIUM
	127 HR VOL. %	275 HR VOL. %	356 HR VOL. %	400 HR VOL. %	
H <sub>2</sub>	74.18	74.64	74.68	75.7	74.1
CO	0.1	0.1	0.22	0.25	0.2
CO <sub>2</sub>	25.38	24.73	24.35	23.5	25.4
CH <sub>4</sub>	0.02	0.46	0.007	-	0.26

## NOTE:

- \* Equilibrium at 204°C (400°F) 59 psig, using effluent from reformer shown in Table 6.2.2D.

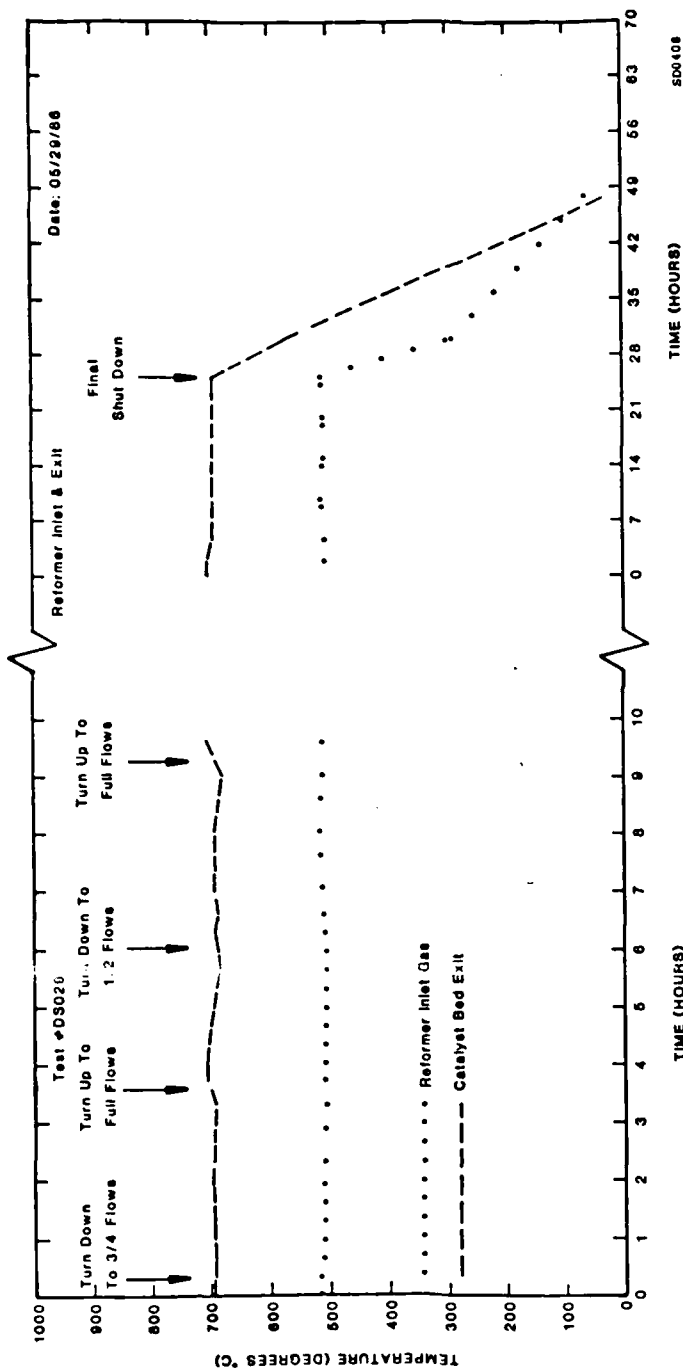
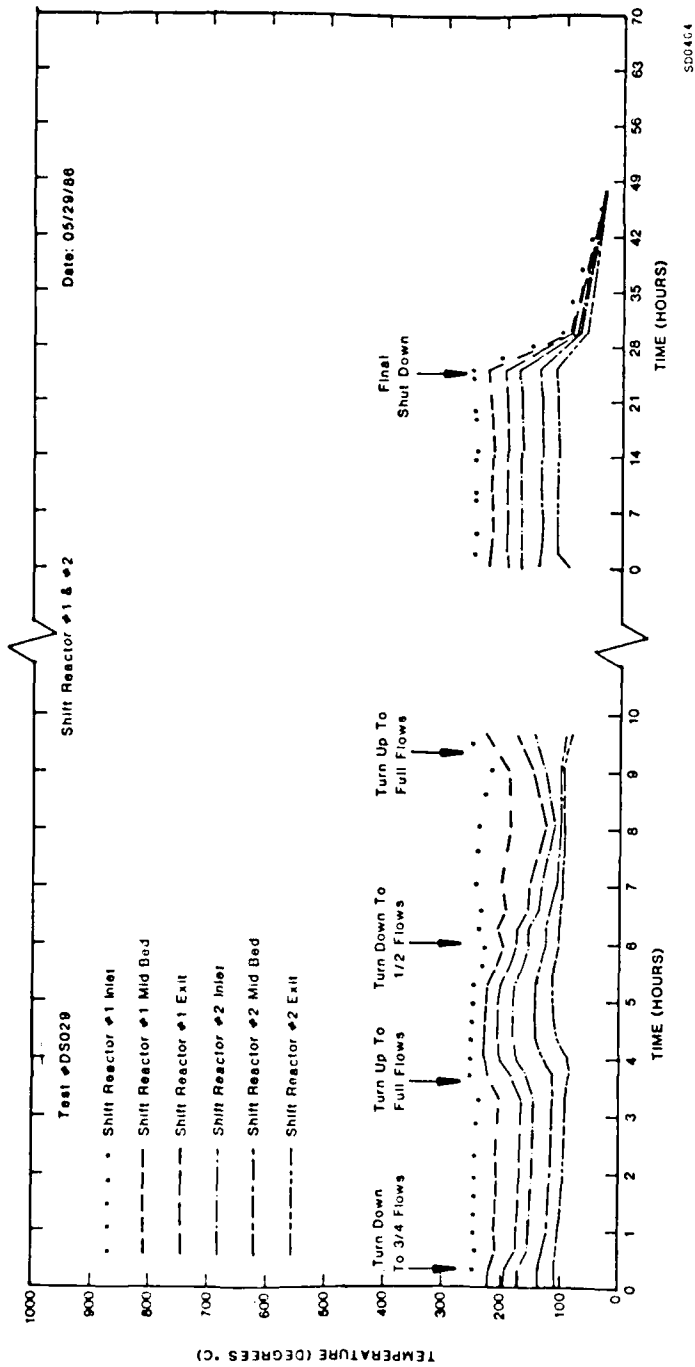


FIGURE 6.2.3A  
REFORMER INLET AND EXIT GAS TEMPERATURE PROFILE  
DURING TRANSIENT TESTING



SD04G4

FIGURE 6.2.3B  
SHIFT REACTOR TEMPERATURE PROFILE  
DURING TRANSIENT TESTING

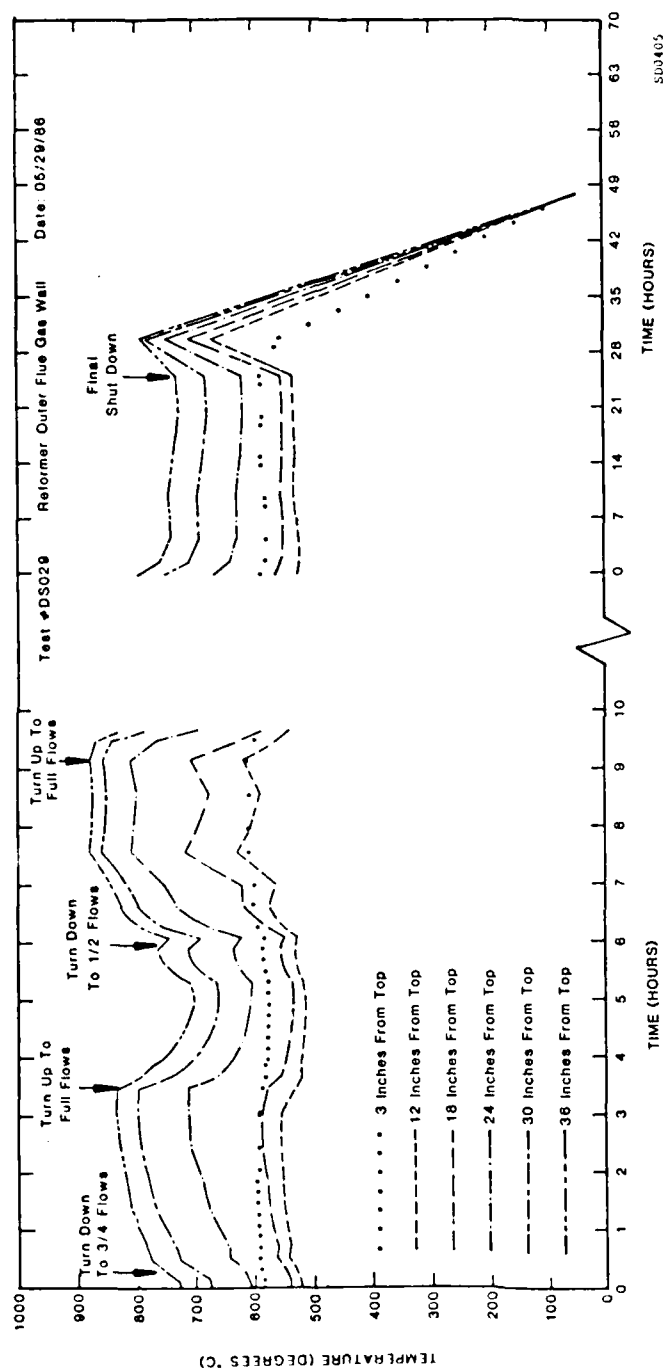


FIGURE 6.2.3C  
REFORMER CATALYST WALL TEMPERATURE PROFILE  
DURING TRANSIENT TESTING

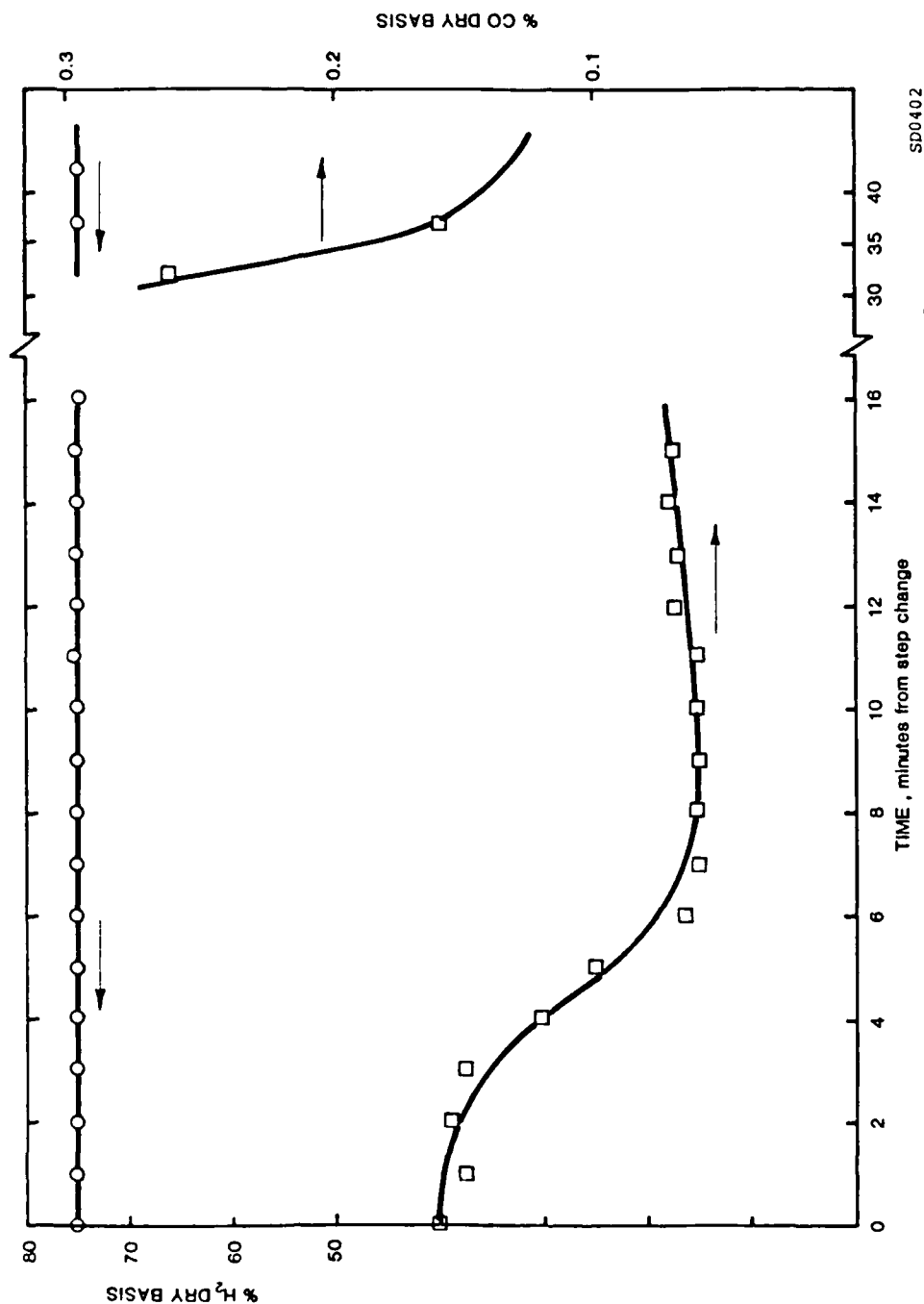
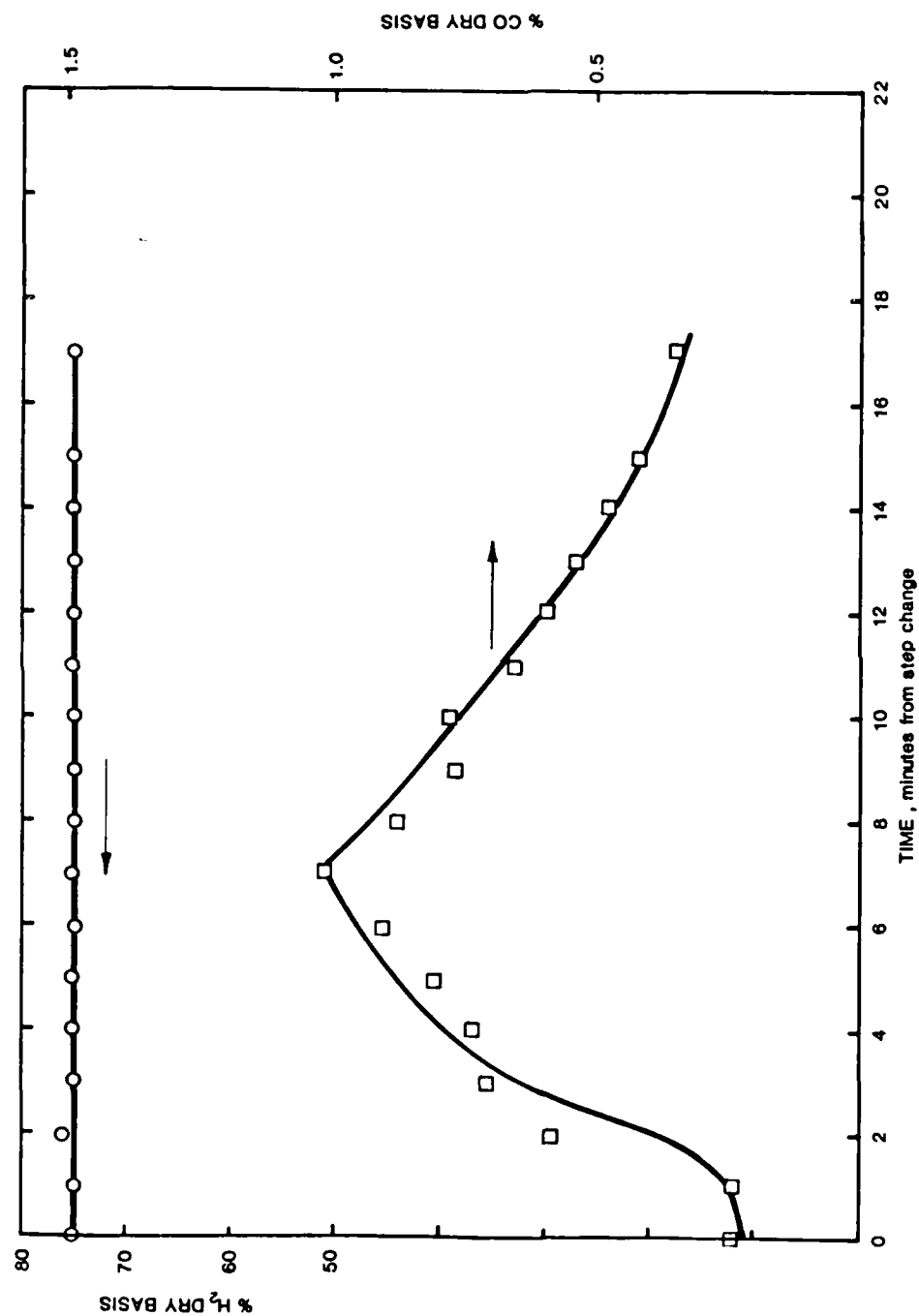


FIGURE 6.2.3D  
EFFECT OF TRANSIENT FROM FULL FLOW TO 3/4 FLOW  
ON FUEL PROCESSOR EXIT GAS COMPOSITION



SD0399

FIGURE 6.2.3E  
EFFECT OF TRANSIENT FROM 3/4 FLOW TO FULL FLOW  
ON FUEL PROCESSOR EXIT GAS COMPOSITION



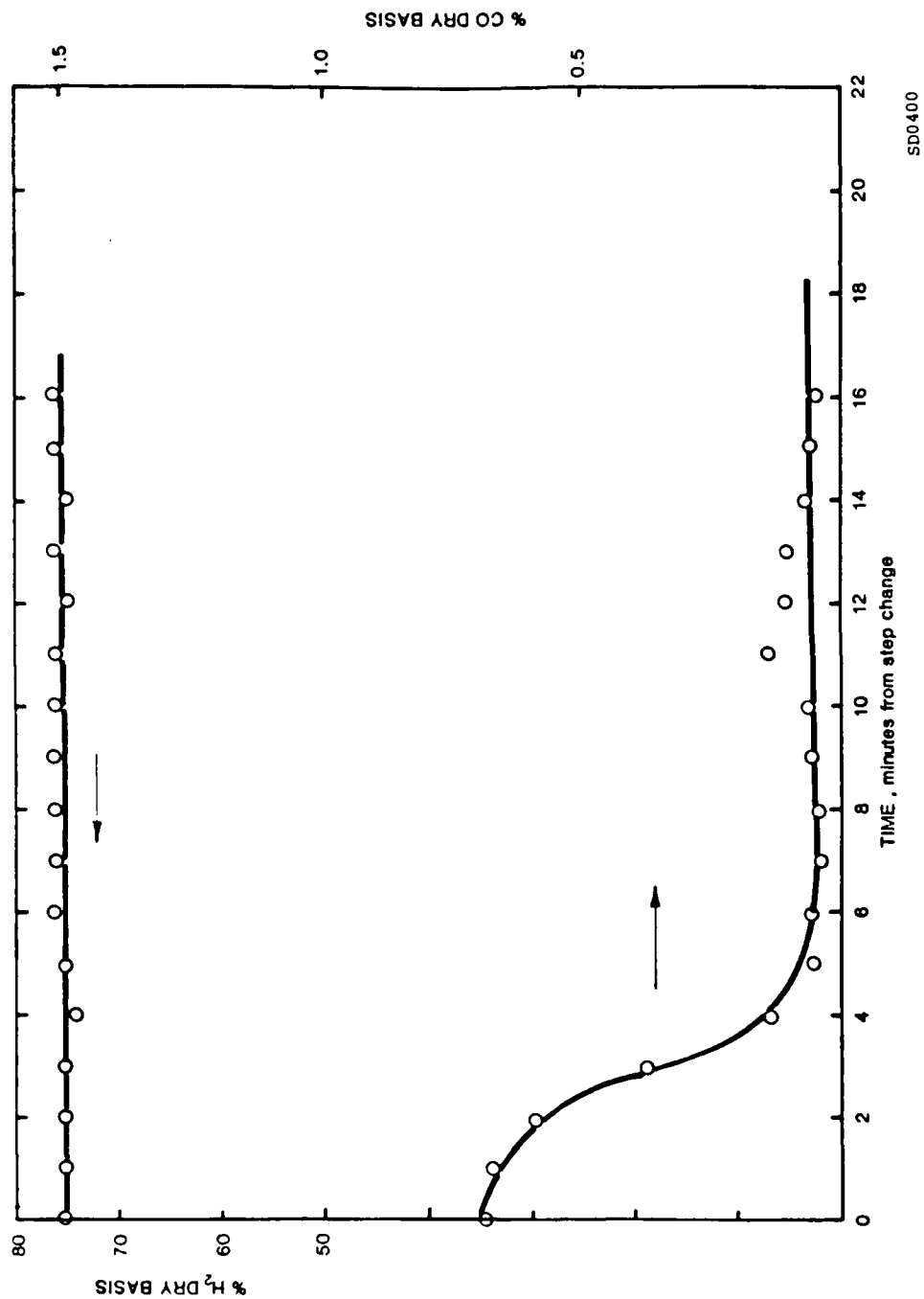


FIGURE 6.2.3F  
EFFECT OF TRANSIENT FROM FULL FLOW TO 1/2 FLOW  
ON FUEL PROCESSOR EXIT GAS COMPOSITION

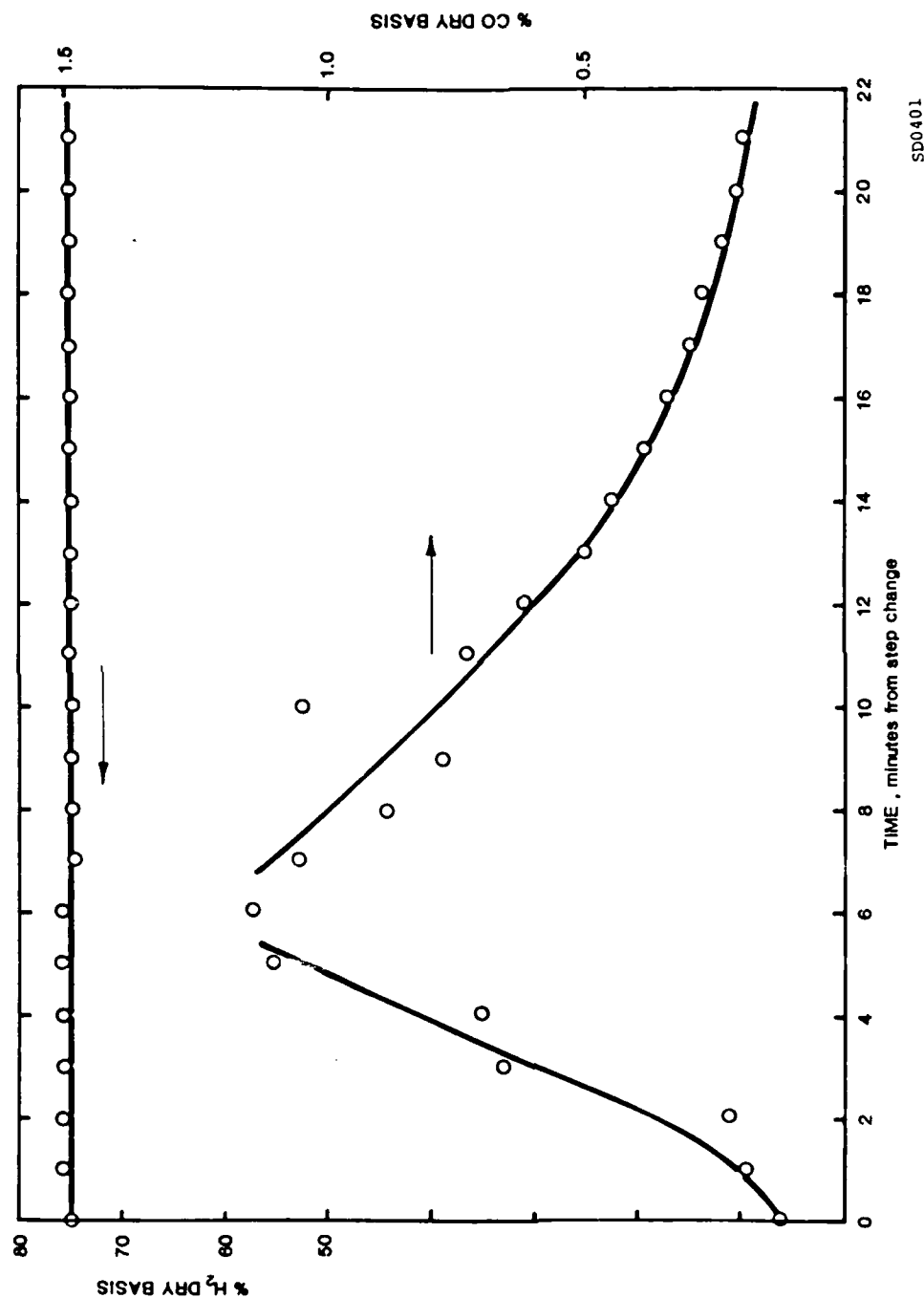


FIGURE 6.2.3G  
EFFECT OF TRANSIENT FROM 1/2 FLOW TO FULL FLOW  
ON FUEL PROCESSOR EXIT GAS COMPOSITION

was done on line. The response time reflected in this data may not represent the response in a power plant accurately due to the lag-time for gas to reach the analyzer, however, a relative indication can be obtained. The step change to 3/4 flow showed no change in hydrogen concentration, but the CO level dropped initially. The reduction in CO is attributed to a simultaneous reduction in temperature in the shift reactor which pushes the equilibrium to lower levels initially. The CO level came back up after about 30 minutes. The transient from 3/4 flow back up to full flow resulted in a sharp increase of CO (up to about 1%), with a gradual decrease towards the normal operating range. The rise in CO occurs with a rise in temperature which affects the equilibrium adversely, causing a higher CO level. The hydrogen is unaffected by the upwards transient.

Transient to 1/2 flow is a little more dramatic in terms of CO content. The CO level drops to a very low level, again due to a temperature drop, while the hydrogen is unaffected. The upwards transient from 1/2 to full flow results in a CO spike of 1.15% which gradually decays to normal levels after about 30 minutes. This level of CO is above the 1% specification and is not desirable, but considered tolerable.

#### 6.2.4 Material Balance

The material balance for the process demonstration test is shown in Table 6.2.4. Stream numbers refer to the process flowsheet (#83035559) shown in Figure 6.2.4. A carbon balance shows a closure of 95.62%. This is considered reasonable considering the accuracy of measurement of flows and compositions.

### 6.3 CARBON DEPOSITION TESTS

Carbon deposition tests were conducted with desulfurized diesel fuel at H<sub>2</sub>O/C ratios of 5 and 4, with short periods of testing at H<sub>2</sub>O/C of 6-8. Due to mechanical problems and time

TABLE 6.2.4

## PROCESS DEMONSTRATION TEST MATERIAL BALANCE

STREAM	1 DIESEL FUEL SUPPLY		2 STEAM BOILER INLET		3 HYDROGEN RECYCLE		4 SECOND STAGE HDS EXIT		5 HDS SYSTEM EXIT		6 STEAM BOILER EXIT		7 REFORMER INLET		8 BURNER AIR	
	lb mole Hr	Vol %	lb mole Hr	Vol %	lb mole Hr	Vol %	lb mole Hr	Vol %	lb mole Hr	Vol %	lb mole Hr	Vol %	lb mole Hr	Vol %	lb mole Hr	Vol %
COMPONENT																
H <sub>2</sub>					.0289	73.9	.025	56.05	.025	56.18			.025	4.96		
H <sub>2</sub> O			.4598	100			.004	8.97	.004	8.99	.4598	100	.4638	91.97		
CO							.004	8.97	.004	8.99			.004	.79		
CO <sub>2</sub>					.0102	26.1	.006	13.46	.006	13.48			.006	1.19		
O <sub>2</sub>															.3885	21
N <sub>2</sub>															1.4615	79
CH <sub>4</sub>																
DIESEL	.0055	98.2					.0055	12.33	.0055	12.36			.0055	1.09		
SULFUR	.1E-03	1.8					.1E-03	.22	4E-08	9E-05			4E-08	8E-06		
TOTAL	5.6E-03	100	.4598	100	.0391	100	.0446	100	.0445	100	.4598	100	.5043	100	1.85	100
TEMP °F	70		70		70		700		700		1375		950		70	
PRESSURE psig	650		30		700		12		12		12		12		43	

TABLE 6.2.4 (concluded)  
PROCESS DEMONSTRATION TEST MATERIAL BALANCE

STREAM	BURNER HYDROGEN 9		BURNER FLUE 10		REFORMER EXIT 11		SHIFT INLET 12		SHIFT EXIT 13		CONDENSER EXIT 14		DRY EXIT GAS 15		CONDENSATE 16	
	lb mole Hr	Vol %	lb mole Hr	Vol %	lb mole Hr	Vol %	lb mole Hr	Vol %	lb mole Hr	Vol %	lb mole Hr	Vol %	lb mole Hr	Vol %	lb mole Hr	Vol %
H <sub>2</sub>	.36	100			.227	34.94	.227	34.94	.262	40.32	.262	40.32	.262	74.07		
H <sub>2</sub> O			.36	17.73	.333	51.25	.333	51.25	.298	45.87	.298	45.87	.002	.6	.296	100
CO					.033	5.08	.033	5.08	.0005	.09	.0005	.09	.0005	.14		
CO <sub>2</sub>					.0565	8.70	.0565	8.70	.089	13.69	.089	13.69	.089	25.16		
O <sub>2</sub>			.2085	10.27												
N <sub>2</sub>			1.4615	72.00												
CH <sub>4</sub>					.0002	.03	.0002	.03	.2E-03	.03	.2E-03	.03	.2E-03	.05		
DIESEL																
FUEL OIL					4E-08	6E-06	4E-08	6E-06	4E-08	6E-06	4E-08	6E-06	6E-06	2E-05		
TOTAL	.36	100	2.03	100	.6497	100	.6497	100	.6497	100	.6497	100	.3537	100	.296	100
TEMP OF		70		1265		900		482		225		77		77		77
PRESSURE psia		40		0		10		10		6 (estimate)		.5		.5		.5

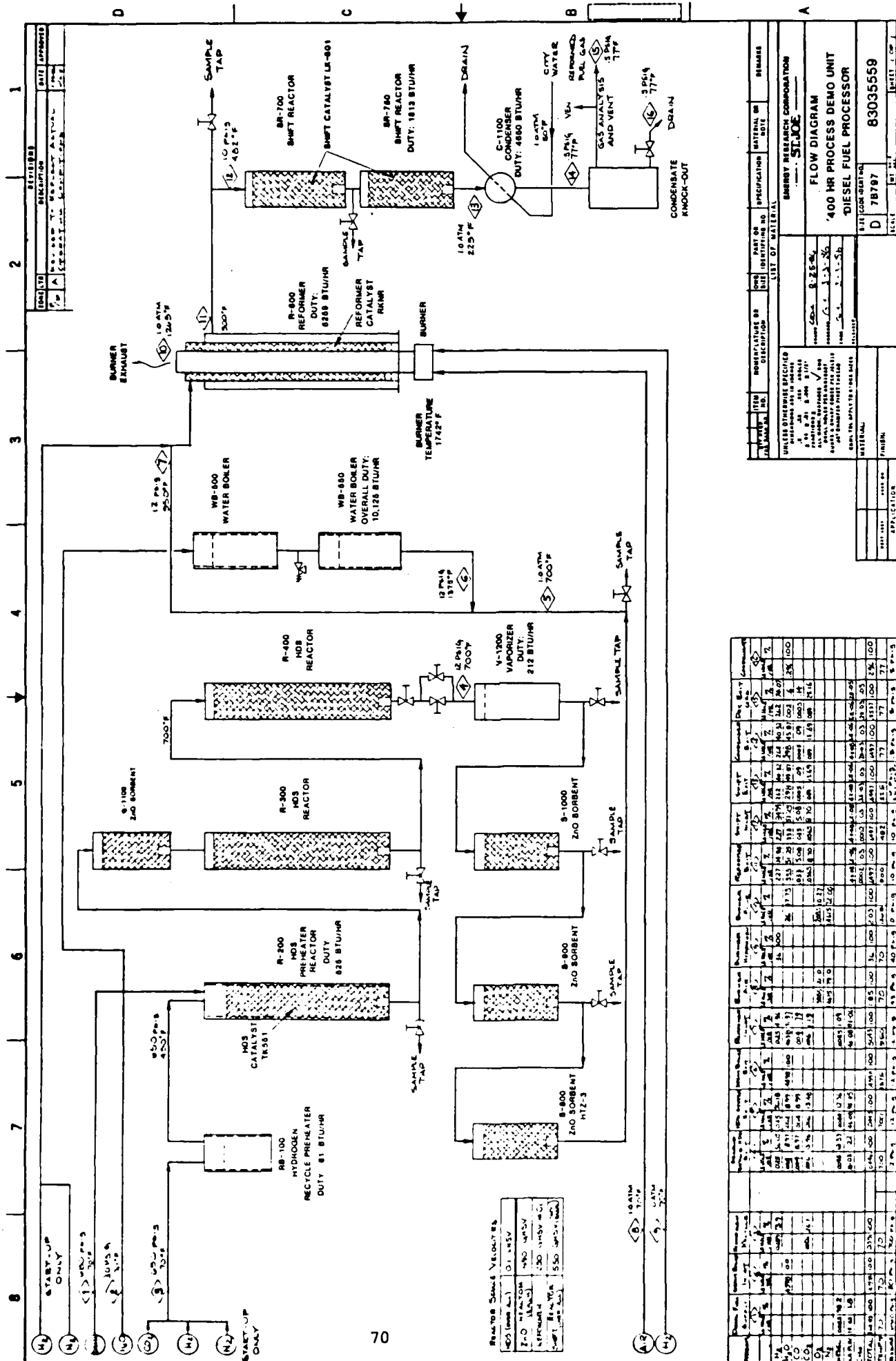


FIGURE 6.2.4

PROCESS FLOWSHEET

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limitations, additional points were not obtained in the determination of carbon boundaries.

Although testing time was not sufficient to determine the minimum  $H_2O/C$  ratio at test conditions, it was demonstrated that operation at  $H_2O/C=4$  or above is possible. No serious deactivation from encapsulating gum was detected, and no whisker carbon was formed.

### 6.4 POST TEST ANALYSIS

#### 6.4.1 Analysis of Catalysts

Post test analysis of catalysts used in the 400-hour demonstration test was conducted and the results indicate the following.

##### 6.4.1.1 HDS Catalyst

The three HDS reactors (one in the first stage, and two in the second stage) were sampled at inlet, mid-bed, and exit of each reactor. This batch of catalyst, installed at about the 300 hour point in the demonstration test, accumulated 170 hours of operation by being tested separately for several days, and then used to complete the 108 hours to the end of the test.

Table 6.4.1.1A shows the analysis obtained. A reduced sulfur level at the inlet indicates that the catalyst was desulfided causing reduced activity there. This is believed to be due to the  $CO_2$  present in the hydrogen recycle stream. The remaining samples indicate good sulfur levels and therefore acceptable activity.

The carbon content of 5-8% is considered high in comparison to VGO (vacuum gas oil) desulfurization, and to testing with diesel fuel and pure hydrogen recycle at 100 atmosphere pressure. The carbon and sulfur levels for these tests are shown in Table 6.4.1.1B.

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TABLE 6.4.1.1A  
HDS CATALYST ANALYSIS AFTER 170 HOURS OF OPERATION

POSITION IN BED	REACTOR #	%C	%S
Inlet	200	7.2	2.3
Middle	200	6.2	5.5
Exit	200	5.8	6.3
Inlet	300	4.7	5.4
Middle	300	5.6	5.9
Bottom	300	6.9	6.1
Inlet	400	6.6	6.0
Middle	400	7.4	5.8
Bottom	400	8.1	6.2

Catalyst: TK 551  
 Recycle H<sub>2</sub>: 500 Nl/l/hr  
 Recycle Composition: 74% H<sub>2</sub>, 26% CO<sub>2</sub>  
 Pressure: 650 psig



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TABLE 6.4.1.1B  
HDS CATALYST ANALYSIS

TIME ON STREAM	POSITION	%C	%S
1132 Hours	Inlet	1.90	6.1
	Exit	1.69	5.7
1268 Hours	Inlet	1.59	6.1
	Exit	1.96	6.3

Catalyst: TK 550  
H<sub>2</sub> Recycle: 500 Nl/Kg/Hr  
Recycle Composition: 100% H<sub>2</sub>  
Pressure: 100 atm

The testing at Topsoe indicates that operation with pure  $H_2$  at 100 atm results in less than 2% carbon after almost 1300 hours. This may indicate that the presence of  $CO_2$  in the recycle stream may be the cause of partial desulfiding at the inlet, and the higher than normal carbon levels.

#### 6.4.1.2 Reforming Catalyst

The reforming catalyst removed after the 400 hour demonstration test was analyzed for carbon, sulfur, reduced nickel and acid soluble nickel. These tests were conducted after the catalyst had accumulated a total of 406.5 hours. However, the catalyst was regenerated at the 298 hour point, so that this analysis is an indication of performance since the regeneration, as well as the effectiveness of the regeneration. Table 6.4.1.2 depicts the results obtained.

The data indicates a slightly sulfur poisoned inlet as expected. The carbon content is very low in all samples, indicating that not only was the regeneration successful, but that the 108 hours of operation after the regeneration were completed without carbon formation. SEM analysis of the used catalyst samples revealed no whisker carbon.

Three samples (top, middle, and bottom) were analyzed for reduced nickel content. The top sample was found to have 17.6% while the middle and bottom were about 23%.

A fully reduced catalyst should have 23-24% reduced nickel. This indicates that the temperature at the inlet of the reactor had not been high enough to completely re-reduce the catalyst after the regeneration.

The powder from the bottom of the reactor was found to be of approximately the same composition as fresh catalyst. It is believed that the powder was formed during the carbon laydown

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TABLE 6.4.1.2  
REFORMING CATALYST ANALYSIS

POSITION	ppm S	%C	% REDUCED NICKEL	ACID-SOLUBLE NICKEL
Top	210	≤0.1	17.6	-
Upper Mid	170	<0.1	-	-
Middle	140	<0.1	22.8	-
Lower Mid	100	<0.1	-	-
Bottom	120	<0.1	23.3	-
Powder	-	<0.1	-	29.9

experienced immediately before the regeneration. During regeneration any carbon present in the powder was oxidized, leaving the composition of the powder virtually like fresh catalyst.

The ethane activity was measured on four samples down through the catalyst bed and it was found that the activity is stable. The activity level is somewhat lower than for the used catalyst from the HTAS testing, but still within the range normally found for used catalyst.

In case of serious deactivation from gum, we would have expected a lower activity of the top catalyst since gum formation is predominant at low temperatures. The S-capacity is found to be significantly lower than seen in the used catalyst from the HTAS tests. The reason for this is believed to be the fact that the catalyst has been through a regeneration during which some sintering is expected. The lower S-capacity also explains that the measured ethane activity generally is lower than for the catalyst from the HTAS test.

#### 6.4.1.3 Shift Catalyst

The used LTS catalyst from the 400 hour demonstration test has been analyzed and the results are summarized in Table 6.4.1.3. As expected, the sulphur level of the inlet catalyst layer is quite high. It is somewhat higher than the chemisorption capacity for LK-801, indicating that the  $H_2S$  concentration in the gas phase has been higher than the equilibrium concentration over  $ZnO/ZnS$ . At  $204^{\circ}C$  and an O/C ratio at the inlet of the reformer of 5.5, the equilibrium concentration of  $H_2S$  is about 5 ppb. This high sulfur level must have been accumulated mostly in the first 298 hours of operation when 10-50 ppm sulfur was fed to the reformer.

Chlorine, which is a serious poison for the LTS catalyst, was also detected on the inlet catalyst layer. Since we expect no

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TABLE 6.4.1.3  
SHIFT CATALYST ANALYSIS

POSITION	ppm S	ppm Cl
1st Bed Inlet	5560	200
1st Bed Upper Mid	25	20
1st Bed Exit	20	10
2nd Bed Exit	45	10

## 6.4.2.3 Shift Catalyst

Typical shift catalyst life is five years of operation. This catalyst life is dependent on the catalyst volume specified for the particular application and the levels of sulfur and chloride expected. Preliminary estimates based on sizing of a scaled-up system indicate a catalyst life of five years for high temperature shift low temperature shift.

6.4.3 Effect of Maximum Sulfur in Fuel

Testing during this program was conducted with diesel fuel containing approximately 0.25 wt% sulfur. The military specification for DF-2 allows a maximum of 0.5 wt% for the continental U.S. and 0.7 wt% outside the continental U.S. The effect of this higher level of sulfur had to be projected.

Based on the kinetic rate expression:

$$- \frac{dC}{dt} = K_n C^n \quad \text{where } n = 1.6 \text{ as determined experimentally}$$

It was determined that the effect of the maximum sulfur levels of 0.5 wt% and 0.7 wt% is small in terms of catalyst bed size required or space velocity considerations. The catalyst volume can therefore be determined by the rate expression used during the test program. The sizing of the larger scale power plant fuel processor sulfur removal section can therefore be determined based on the sulfur level tested, and no additional consideration is required for higher sulfur fuels within the mil-spec limits.

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## 7.0 RELIABILITY ANALYSIS

To demonstrate the feasibility of the FPS for producing a hydrogen rich stream, a 406.5 hour test was run. This test was monitored carefully not only to determine that a desired fuel conversion rate was met, but that it was at least potentially capable of a satisfactory level of dependability over a significant period of time (400 hours). The goal for fuel conversion expressed in terms of a fractional pound of fuel cell quality hydrogen per pound of DF2 Diesel Fuel is in the range of 0.365 pound H<sub>2</sub> for each pound of Diesel Fuel, minimum acceptable, to 0.420 pound H<sub>2</sub> for each pound of Diesel Fuel, maximum theoretical. 0.39 lb H<sub>2</sub> was realized for each pound of Diesel Fuel required during the 406 hour test. This result is considered complete conversion of the diesel fuel.

This test had other goals that were exceeded by significant margins. The gas output from the FPS was found to have a hydrogen constituent of 74% when the goal was to exceed 50%. Only 0.2% (by volume) of CO was observed, when the goal was to restrict the quantity of CO to less than 1%. Another goal was to restrict the quantity of sulfur to less than 10 parts per million by weight. The FPS was able to hold the amount of sulfur down to less than 1 part per million by weight.

Since reliability has been defined as the probability that a device will provide its desired function for an extended period of time, an initial level of reliability has been established. During the 406.5 hours of test, eight (8) malfunctions were observed (see Appendix 4). These eight (8) were reviewed in depth. Four of the eight were leaks, one was an operational problem that required shut-down but no repair action, one was an electrical intermittent failure that recovered spontaneously with no intervention, and one was a short-circuited thermocouple. Only one of the eight appeared to require a design change.



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The design change indicated is to be implemented in future applications. Thermocouples will be made redundant in the future so that significant differences within a redundant pair can be monitored. The leaks were attributed to cyclical contractions and expansions of system components. In future FPS the number of connections and fittings will be reduced significantly, or made permanent through welding. The system under test was deliberately constructed to make it easy to remove and replace components that would otherwise remain fixed for thousands of hours in a commercial operating environment. All the observed leaks were in the high pressure, high temperature portion of the FPS.

The equipment used in the feasibility study was not designed with single point failures specifically in mind. In most cases, the failure of a component would shut the system down. Of course in an experimental test such as this with much data being collected from numerous instruments, the loss of a particular device would not be expected always to result in system shut-down. Redundancy would be present in the form of duplicate information. This comment is applicable most specifically to measurement and control devices. The feasibility study and test under this contract has established the fact that hydrogen of a quality suitable for fuel cell use can be produced for significant periods of time. The FPS has been demonstrated to function reliably. The observed malfunctions were of a nature that they can be eliminated completely, or at worst, reduced to a very low level, with minor design improvements or improved manufacturing procedures not appropriate to a test facility. When the current design is scaled-up to produce at least 100 kW, the elimination of single point failures will be a major design goal. This is an absolute necessity to assure that reliability, i.e. MTBF requirements be met. Ideally, no one component failure should result in system failure (complete loss of power output). This ideal situation may not be achievable at this time and state-of-the-art, when life cycle costs must be minimized.

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Current data does not indicate that reliability is likely to be a function of plant size. Gerald P. Williams of Allied Corporation Hopewell, Virginia and William W. Hoehing, Exxon Chemical Company, Florham Park, New Jersey in a paper presented to the American Institute of Chemical Engineers (AIChE Paper No. 124g - Nov. 82) "Causes of Ammonia Plant Shutdowns - Survey IV" indicated that size of plant over a broad range did not appear to affect reliability. Ammonia plants are suggested for comparison due to the similarities in the equipment used to produce hydrogen. Instead of a reduction in reliability postulated for a full scale 100 kW power plant, it would appear that the design engineers developing the larger power plant should produce no worse reliability than observed for the present feasibility model.

The study of ammonia plants further indicated that plant shutdowns occurred on average about every 1168 hours (MTBF) and overhaul was about every 10,600 hours calendar time (9400 hours operating time). The power plant incorporating the FPS has projected requirements of approximately four times this - MTBF of 4,000 hours and overhaul at 5 years (43,800 hours). The ammonia plants considered in this study had startup dates between 1965 and 1980, so there has been an extensive time period for eliminating reliability problems.

### 7.1A RELIABILITY PREDICTION BASED ON 406.5 HOUR TEST

A power plant having a true MTBF of 4000 hours, will require a 9220 hour test with no failures to provide 90% confidence that this result has been achieved. To provide 95% confidence that 4000 hours MTBF has been achieved would require 12,000 hours of testing with no relevant failures. A test of 406.5 hours with no failure will give 5% confidence that a 7925 hour MTBF has been achieved and a 10% confidence level that an MTBF of 3858 hours has been achieved. A 4000 hour test with no failure would provide a 62.3% confidence level (probability) that the true MTBF exceeds

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4000 hours. The 406.5 hour test performed under this contract was limited to the FPS. None of the eight malfunctions observed was judged to be inherent in the FPS design, but were a function of the limitations of the test facility. With no relevant failures in the equipment under test and the government interest in an MTBF of 4000 hours, the 10% confidence level was chosen. This indicates demonstration of 3858 hours at 10% confidence. At this stage there is a 10% probability that the true MTBF exceeds 3858 hours. Additional test time with no failures will increase this confidence level, or increase the demonstrated MTBF without increasing the confidence level.

### 7.1B RELIABILITY PREDICTION BASED ON ESTIMATED COMPONENT MTBF

The fuel processing system conceptually has been divided into ten sub-systems of which eight are different. The fuel delivery system and Shift Reactors are replicated. Historically, non-electronic components have not received the attention that electronic parts have received in terms of reliability data gathering. When data for non-electronic components can be found it is subject to greater variability, and predictions for the individual piece-parts are subject to greater error. For fuel cells few piece-parts and components have failure rates that are known with any degree of precision unless they have been produced in significant quantities for other purposes. Many fuel cell components are quite unique, one of a kind, or produced in rather small quantities with very little track record. And yet, it is useful to put together a reliability prediction for assemblies of these piece-parts. Such a prediction has been put together for the diesel fuel processor system in Table 7.1. The actual failure rates have varying levels of validity. Some are based on a manufacturer's claim for his product where he may have collected an indeterminate amount of operational data and some are based to a significant extent on engineering judgement. Not all piece-parts are listed unless they are expected to result in relevant failures, when they do fail. The "best" available

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TABLE 7.1  
DIESEL FUEL PROCESSOR SYSTEM RELIABILITY PREDICTION

	Failures/ 10 <sup>6</sup> Hours $\lambda$	Meantime Between Failures (hours) M	Failures/ 20 Years
<u>Fuel Delivery System #1</u>			
Pump	28.52	35,063	5.00
Filter	2.24	446,429	0.39
Tank & Fittings	4.71	212,314	0.83
	35.47	28,193	6.22
<u>Fuel Delivery System #2</u>	35.47	28,193	6.22
<u>Sulfur Removal System</u>			
HDS (2 @ 102.5)	205.00	4,878	35.94
ZnO (2 @ 102.5)	205.00	4,878	35.94
	410.00	2,439	71.88
<u>Low Pressure Reformer</u>			
Burner	17.11	58,445	3.00
Catalyst Bed	102.50	9,756	17.97
Vessel	1.00	1,000,000	0.18
	120.61	8,291	21.15
<u>High Pressure Reformer</u>			
Burner	17.11	58,445	3.00
Catalyst Bed	102.50	9,756	17.97
Vessel	1.50	666,667	0.27
	121.11	8,257	21.24
<u>Shift Reactor #1</u>			
Catalyst Bed	101.00	9,901	17.71
Vessel	1.00	1,000,000	0.18
	102.00	9,804	17.89
<u>Shift Reactor #2</u>	102.00	9,804	17.89
<u>Water Treatment</u>			
Deionizer	10.00	100,000	1.75
Deaerator	10.00	100,000	1.75
	20.00	50,000	3.50
<u>Water Delivery System</u>			
Tank w/Fittings	4.48	223,214	0.79
Pump	17.11	58,445	3.00
	21.59	46,318	3.79
<u>Heat Exchanger</u>			
1 H.X.	7.00	142,857	1.23
15 Other H.X.	105.00	9,528	18.41
	112.00	8,928	19.64
	1,080.25	925	189.40

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TABLE 7.1 (concluded)

DIESEL FUEL PROCESSOR SYSTEM RELIABILITY PREDICTION

Failures in 406.5 Hours	Probability of Failure	Cummulative Probability of Failure
0	0.6446	0.6446
1	0.2831	0.9277
2	0.0621	0.9898
3	0.0091	0.9989
4	0.0010	0.9999
<hr/>		
$\frac{-406.5}{924.7} = -0.43912$		
70.94	12.44	$P(0) = 3 = e = 0.6445988156$
410.00	71.88	$P(1) = 0.2830608389$
120.61	42.37	$P(2) = 0.0621498493$
121.11	35.78	$P(3) = 0.0090972286$
204.00	7.29	$P(4) = 0.00099871$
20.00	19.63	
21.4 <sup>a</sup>	189.42	
112.00		
1,080.25		

## ENERGY RESEARCH CORPORATION

failure rate is assigned to each part and these are combined to estimate a failure rate for each of the eight functions defined for the Diesel fuel processor system. The failure rates of each of the eight functional subsystems in turn are combined to provide a failure rate estimate for the complete diesel fuel processor system. The mean-time-between failures is given at each functional level to give a feeling for the frequency of failure in the time domain. The third column (see Table 7.1) gives an estimate of the manner in which the numbers of failures for a 20 year equipment life might be distributed. This should be of significant value in planning for maintainability and spares provisioning on a preliminary basis.


A MTBF estimate of 925.7 hours was obtained for the complete system. For the 406.5 hour test that implies 0.44 failure was expected. This in turn implies a probability of 64.46% for no failures, 28.31% for one failure, 6.21% for two failures and 0.91% for three failures. There should only be about one chance in a thousand of having more than three failures.

### 7.2 RELIABILITY APPORTIONMENT TO MEET 4000 MTBF

Current predictions indicate that a MTBF in the area of 925 hours might be expected for the Diesel Fuel Processor System. This does not appear adequate when the FPS must be combined with fuel cell stacks and other equipment to form an electric power generating plant.

Assuming design with a strong emphasis on reliability would increase the MTBF by a factor of four or somewhat more a possible goal of 4,000 hours was set. This MTBF corresponds to a failure rate of 250 failures per million hours (FPMH). Table 7.2 indicates that the relative complexities were determined by engineering judgement. Weight factors were then assigned on a scale on one to ten. The 250 FPMH were divided up in ratio to the projected complexity. The numbers thus determined were

TABLE 7.2  
RELATIVE COMPLEXITY OF DIESEL FUEL PROCESSOR SYSTEMS

	WEIGHT FACTOR	INCREASING COMPLEXITY
Heat Exchanger	1	
Shift Reactor	2	
Water Treatment	4	
Water Delivery	5	
Fuel Delivery	5	
Low P Reformer	7	
High P Reformer	9	
Sulfur Removal	10	

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divided again in the same manner for the components of each subsystem. These divided and subdivided failure rates are listed in Table 7.3. The reciprocal of each failure rate was computed for Table 7.3. Since 20 years has 175,321.2 hours, this number was divided by these reciprocals (MTBF) to estimate the number of failures one might expect in 20 years.



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TABLE 7.3

## DIESEL FUEL PROCESSOR SYSTEM RELIABILITY APPORTIONMENT

	$\lambda \times 10^6$	MTBF	Failure/ 20 Years
<u>Fuel Delivery System #1</u>			
Pump	15.24	65,626	2.67
Filter	0.27	3,740,683	0.05
Tank & Fittings	3.72	286,470	0.65
	19.23	52,002	3.37
<u>Fuel Delivery System #2</u>	19.23	52,002	3.37
<u>Sulfur Removal System</u>			
HDS (2 @ 12.82)	25.64	39,001	4.50
ZnO (2 @ 6.41)	12.82	78,003	2.25
	38.46	26,001	6.75
<u>Low Pressure Reformer</u>			
Burner	18.94	52,798	3.32
Catalyst Bed	9.47	105,597	1.66
Vessel	1.89	529,101	0.33
	30.30	33,003	5.31
<u>High Pressure Reformer</u>			
Burner	18.94	52,798	3.32
Catalyst Bed	9.47	105,597	1.66
Vessel	2.87	352,112	0.50
	31.25	32,000	5.48
<u>Shift Reactor #1</u>			
Catalyst Bed	4.32	229,885	0.76
Vessel	3.34	299,401	0.59
	7.69	130,039	1.35
<u>Shift Reactor #2</u>	7.69	130,039	1.35
<u>Water Treatment</u>			
Deionizer	7.69	130,039	1.35
Deaerator	7.69	130,039	1.35
	15.38	65,020	2.70
<u>Water Delivery System</u>			
Tank w/Fittings	4.81	207,900	0.84
Pumps	14.42	69,348	2.53
	19.23	52,002	3.37
<u>Heat Exchangers</u>			
1 H.X.	3.85	259,740	0.67
15 Other H.X.	57.75	17,316	10.13
	61.60	16,233	10.80
	250.06	4,000	43.85

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### 8.0 CONCLUSIONS

A process demonstration test was conducted in which the proposed process was tested for 406.5 hours. A summary of the program requirements and accomplishments is shown in Table 8.0.

#### 8.1 SULFUR REMOVAL

A critical aspect of this process demonstration was the sulfur removal system. Initially it was anticipated that sulfur removal could be accomplished at the operating pressure of the fuel cell and the remainder of the fuel processor, namely atmospheric pressure. Multiple staged HDS/ZnO systems were tested, and it became apparent that at low pressures (atmospheric to 100 psig) the desulfurization activity is not sufficiently high to achieve the required sulfur removal. It therefore was necessary to increase the operating pressure of the HDS in order to achieve the degree of sulfur removal required. Testing at ERC at 650 psig with  $H_2/CO_2$  recycle gas demonstrated that sulfur removal to less than 1 ppm can be achieved with diesel fuel. Testing at ERC with pure  $H_2$  and 100 atmospheres pressure showed sulfur removal to 0.1 ppm. Activity with pure  $H_2$  at 100 atm was found to be 72 g mole/liter hr (on Co-Mo) while activity at 650 psig with  $H_2/CO_2$  was found to be about 72 g mole/liter hr. In addition, the sulfur levels with the  $H_2/CO_2$  at 650 psig were relatively stable after 170 hours, while carbon levels with pure  $H_2$  at 100 atm were acceptable at 2 wt%.

An additional disadvantage of the  $CO_2$  shift reaction is that some reverse shift occurs in the HDS which in turn affects the equilibrium with the ZnO, allowing  $H_2S$  leakage of  $H_2S$  from the ZnO. The total sulfur going to the reformer will be increased.

If  $CO_2$  is removed from the reformer, the sulfur from the ZnO can be limited to the level of sulfur in diesel fuel since the equilibrium

AD-A176 443

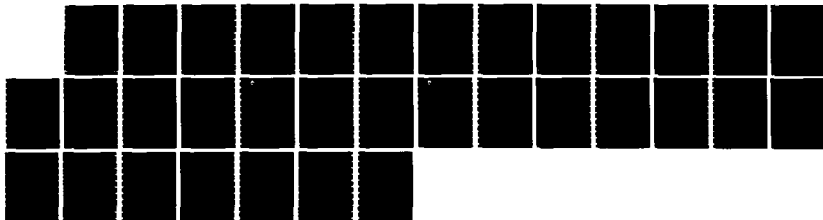
DIESEL FUEL PROCESSING FOR THE PAFC PROCESS  
DEMONSTRATION(U) ENERGY RESEARCH CORP DANBURY CT  
G STEINFELD ET AL 15 DEC 86 DAAK70-85-C-0090

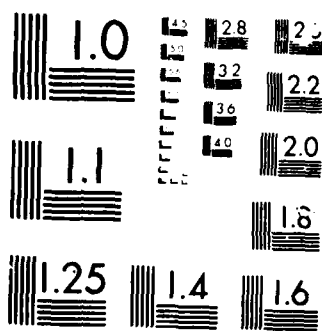
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TABLE 8.0  
DIESEL FUEL CONDITIONER  
CONTRACT REQUIREMENTS AND ACCOMPLISHMENTS

ITEM	CONTRACT REQUIREMENT	ACTUAL DELIVERED
PROCESS DEMONSTRATION	400 Hours	406.5 Hours
PROCESS DEMONSTRATION SIZING	Process to be sized so that it can be scaled up to 200 kW Size	Demonstration test oper- ated at 2.5 kW. Can be scaled up according to commercial practice.
FUEL CONVERSION <u>1b hydrogen</u> <u>1b diesel</u>	0.365 Minimum 0.420 Desired	0.39
SPECIFIED FUEL	DF-2, DF-A, JP-4	Exxon DF-2
FUEL SULFUR LEVEL	5000 ppm Max - Extrapolate results if less than 3500 ppm.	2800 ppm - Effect of 5000 ppm is negligible.
GAS COMPOSITION	H <sub>2</sub> 50 Volume % CO            1 Volume % Sulfur        10 ppmw	H <sub>2</sub> 74 Volume % CO            0.1 Volume % Sulfur        <1 ppmw
TURN DOWN CAPABILITY AND TRANSIENTS	Show effect of 3/4 and 1/2 load and effect of step in- crease or decrease of fuel feed from full to 3/4 and 1/2 load and reverse.	Turn down to 1/4 load and load flows and reverse demonstrated.
CATALYST LIFE	To be projected from test and demonstration data.	Projection provided.
CARBON DEPOSITION BOUNDARIES	Define analytically or experimentally	Determined experimentally H <sub>2</sub> O/C boundary is below 4.
RELIABILITY ANALYSIS	Conduct reliability analy- sis applicable to 100 kW size unit.	Reliability analysis pro- vided.

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Testing at Topsøe indicates that sulfur can be reduced to less than 0.1 ppm at 50 atmospheres using Co-Mo (TK550) and pure H<sub>2</sub> as recycle gas. Using an estimated 0.11 V/V/hr space velocity, the catalyst volume required to process about 90 lb/hr of fuel (nominal 150 kW power plant) would be 15.5 ft<sup>3</sup>. The corresponding volume using H<sub>2</sub>/CO<sub>2</sub> recycle gas using a lower space velocity of .02 V/V/hr would require 85 ft<sup>3</sup> of catalyst. This is a factor of 5.5 increase in volume.

The conclusion is that there is a distinct advantage to providing pure hydrogen to the HDS, however, if that is not possible, additional catalyst volume can be used to overcome the penalty of lower activity in the presence of CO<sub>2</sub>. The resulting additional sulfur leakage may require the reformer to operate at slightly higher temperature and H<sub>2</sub>O/C ratio. In addition, the long term rate of carbon build-up in the HDS catalyst should be determined when using H<sub>2</sub>/CO<sub>2</sub> recycle gas.

### 8.2 REFORMING

Testing and analysis of used catalysts from both ERC's reformer tests and Topsoe's tests indicate that full conversion of desulfurized diesel fuel is achievable at H<sub>2</sub>O/C ratios down to 4.0. No serious deactivation from encapsulating gum was detected and no whisker carbon was formed. The tests conducted were at low pressure (1-2 atmospheres).

The successful reforming tests were conducted with low sulfur (<1 ppm sulfur) diesel fuel. Sulfur reduction to below 0.1 ppm S is preferable for reasonable life at the conditions tested. Higher sulfur may be acceptable if the operating temperature and H<sub>2</sub>O/C ratio are increased.

Regeneration of the reforming catalyst was successfully demonstrated when it was required due to sulfur poisoning, and subsequent carbon formation.

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Cyclical operation when purge gas is used during shutdown and startup does not appear to affect the reformer adversely.

### 8.3 SHIFT

The low temperature shift catalyst performed well throughout the test. Analysis of the catalyst revealed sulfur and chlorine poisoning at the inlet. Cooling at the reactor inlet was inadequate, whereas cooling was excessive at the exit of the first bed.

Since the fuel processor will be self-sufficient with regard to water, it is anticipated that chlorine poisoning will not be a problem in a scaled up power plant. Sulfur poisoning should not occur when the HDS operates properly. However, life expectancy can be increased by incorporating a layer of ZnO at the inlet of the low temperature shift.

The use of a shift system with adiabatic high temperature shift (HTS) and low temperature shift (LTS) will eliminate the problem of controlling catalyst temperatures.

### 8.4 OVERALL FUEL PROCESSOR

The feasibility of generating a fuel cell grade hydrogen stream from diesel fuel was demonstrated in a 400 hour test. Based on the testing to date, preliminary sizing can be determined for a scaled-up power plant.

The fuel processor tested was based on utilization of unused hydrogen from the fuel cell anode as fuel to the reformer burner. This fuel gas was simulated for the purpose of the test, and was not accounted for when calculating the  $\#H_2/\#Diesel$  produced by the fuel processor. When taking the hydrogen used by the reformer burner into account, the  $\#H_2/\#Diesel$  number is lowered to 0.285  $\#H_2$  consumed by the fuel cell per pound of diesel fuel processed, in order to achieve a 40% overall efficiency.

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The high pressure sulfur removal system requires high pressure hydrogen to be supplied to the HDS system. This hydrogen was simulated for the purpose of this process demonstration, but can be supplied by the fuel processor system.

Transient testing indicates negligible effect on measurable parameters, with the exception of CO level. A step increase in flows generates a CO "spike" which is not desirable. Scale-up of the process should include measures to minimize the effect and its consequences on the stack.

### 8.5 RELIABILITY

The reliability analysis conducted based on the data generated indicates that the 400 process demonstration test was not long enough to provide reliability data for long term operation with a high degree of confidence. A 10% confidence level can be calculated for an MTBF of 3858 hours for the fuel processor based on a successful 400-hour test. Longer test periods are required to develop higher confidence levels. For example, to provide 95% confidence that 4000 MTBF has been achieved would require 12,000 hours of testing with no relevant failures.

Based on estimated component MTBF, a 926 MTBF was calculated for the fuel processor. The required MTBF for individual components required to achieve a 4000 MTBF for the fuel processor was calculated as goals for each component.



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## 9.0 RECOMMENDATIONS

It is recommended that testing be conducted in order to verify production of high pressure hydrogen in a diesel fuel processor in a manner compatible with the efficiency and reliability requirements.

Longer term hydrodesulfurization tests with diesel fuel are recommended with  $H_2/CO_2$  recycle gas in order to determine carbon formation levels on HDS catalyst and its effect on long term HDS activity. Trade-offs of purifying hydrogen for HDS recycle should be evaluated.

Additional tests to sulfide and regenerate zinc oxide should be conducted to demonstrate a larger number of cycles of sulfidation/regeneration, as well as to minimize sulfate formation and decomposition. The effect of  $SO_2$  on downstream equipment should be investigated.

With parallel on-going laboratory tests to investigate the above mentioned items, it is recommended that scale-up of this process be initiated. Additional systems analysis should be conducted to determine the options and trade-offs in integrating this fuel processor with the fuel cell stack system, the water recovery, steam generation system, and waste heat recovery.

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APPENDIX 1  
ANALYTICAL METHODS

1-1	GAS ANALYSIS
1-2	SULFUR ANALYSIS
1-3	CATALYST ANALYSIS
1-4	WATER ANALYSIS

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### 1-1 GAS ANALYSIS (ERC)

Analyses of the major components of the reformer exit gas were performed using a Perkin Elmer Sigma 3 gas chromatograph equipped with a thermal conductivity detector and a 10 port heated gas sampling valve. The column configuration consisted of a standard series/bypass arrangement of porous polymer and molecular sieve columns via a four port column switching valve. Peak integration, valve switching, and component concentration reporting was accomplished with a Spectra-Physics SP4100 computing integrator.

Qualitative analyses of trace hydrocarbons in the C<sub>1</sub>-C<sub>7</sub> range contained in the product gas were performed using a stock 23% SP-1700 column installed in a second Perkin Elmer Sigma 3B HWD gas chromatograph. Sample introduction was by syringe, and a strip chart recorder was used to measure and record peaks.

### 1-2 SULFUR ANALYSIS

Desulfurized diesel fuel was analyzed for sulfur by the micro-coulometric method (ASTM D3120), and by Tracor Atlas (ASTM 4045). The liquid fuel is pyrolyzed and hydrogenated to convert all sulfur to H<sub>2</sub>S. The H<sub>2</sub>S level is then detected by photorateometry. This method utilizes a lead acetate impregnated paper sensing tape to cause the surface to darken from lead sulfide formation. The rate of darkening of the exposed tape is proportional to H<sub>2</sub>S concentration. A photorateometry sensing method is used to convert the signal to a meter deflection.

### 1-3 CATALYST ANALYSIS (Haldor Topsoe)

#### Carbon on TK55/RKNR, LEGO

Carbon is determined gravimetrically by weighing the CO<sub>2</sub> produced by combustion of the sample in oxygen. The equipment used is a LEGO Gravimetric Carbon Determinator which has an

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Ascarite (NaOH on asbestos) weighing tower (gravimetric absorption bulb) that absorbs the CO<sub>2</sub> combustion products. The bulb is weighed before and after combustion and the weight increase is CO<sub>2</sub>. The practical lower limit is approximately 0.01% carbon. The accuracy is -0.005% or -1% of the carbon present, whichever is greater.

Sulfur on TK-551/ LK-801/RKNR, Gustafsson

The sample, which contains sulfur in the form of inorganic compounds, is treated with a solution containing sodium hypophosphite in acetic acid/ hydroiodic acid. The inorganic sulfur compounds are reduced to hydrogen sulfide, which is expelled and absorbed. After this the sulfur content is determined by means of a titration with mercury acetate. For very small amounts of sulfur (<25 µg) a calorimetric method can be used alternatively.

Reference: ASTM D 2725-70

Chlorine on LK-801

Chloride ions, which are brought into solution on treating the sample with boiling water or 4N nitric acid, release thiocyanate ions from non-dissociated mercury thiocyanate. The released thiocyanate ions form ferric ions with the red ferric thiocyanate, the concentration of which is measured calorimetrically at 460 nm. A calibration curve is made from the executions of varying known amounts of chloride mixed with mercury (II), thiocyanate and ferrinitrate. A blank made from the reagents must be subtracted. The amount of chloride, corresponding to the extinction of the sample, minus the extinction of the blank, can be found from the calibration curve.

Reference: ASTM 23 (1969) D512-62T, p. 21

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1-4 WATER ANALYSIS

Water analysis was according to standard methods for the examination of water and waste water 16th edition 1985 APHA-AWWA-WPCF.

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APPENDIX 2  
FUEL ANALYSIS



**E.W. SAYBOLT & CO., INC.**

OFFICE West Haven, Ct.

**LABORATORY ANALYSIS REPORT**

CUSTOMER REF. NO.:                      P.O. #E-31853  
DATE: 1-28-86  
VESSEL/TANK(S):                      3630  
LABORATORY NO.:                       
INVOICE NO.: EV-5158

**DESCRIPTION**

Sample designated as:  
Diesel Fuel

Identifying Marks:  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

Submitted by:  
\_\_\_\_\_  
\_\_\_\_\_

Client: Energy Research Company  
\_\_\_\_\_  
\_\_\_\_\_

**NOTES**

- This laboratory report may not be published or used except in full. It shall not be used in connection with any form of advertising unless written consent is received from an officer of E. W. Saybolt & Co., Inc.
- Results were based on analysis made at the time samples were received at the laboratory.
- Samples, if any, shall be retained for a period of 45 days unless a longer period is requested in writing.
- Sample nomenclature is designated by the customer.

**ANALYSIS**

Gravity, API @ 60°F ASTM D-287	35.6°F
Appearance	Clear
BTU Per Pound ASTM D-240	19721
BTU Per Gallon ASTM D-240	139055
Cloud Point, ASTM D-2500	+4°F
Color, ASTM D-1500	Red
Flash Point, ASTM D-93	116°F
Pour Point, ASTM D-97	-15°F
Sulfur, ASTM D-1552	0.28%
Viscosity, SU @ 100°F ASTM D-88	34.2 sec.
Water & Sediment ASTM D-96	0.03%
Initial Boiling Point	334°F
10%	392°F
50%	494°F
90%	596°F
End Point	646°F
Recovery	98.5%
Cetane Index ASTM D-976	45.9

**ANALYSIS OF FUEL USED IN 400-HOUR PROCESS DEMONSTRATION**

MEMBERS ASTM - API - SAE

(203) 934-8391 ml

*Dredging Research*

# ENERGY RESEARCH CORPORATION

CONFIDENTIAL

ST. JOE

6/17/86

Exxon Company, USA  
200 Unicorn Park  
Woburn, Mass. 01801-3390

ATTN: Mr. W.R. Moorman

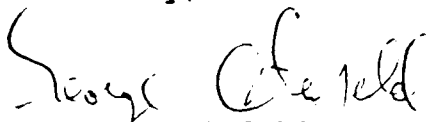
RE: Additives in Diesel Fuel

Dear Mr. Moorman:

We have been conducting tests with Exxon DF-2 for Fuel Cell application this past year. We have been desulfurizing and reforming fuel which we obtained locally through a local vendor in order to produce hydrogen suitable for fuel cell consumption. Although we have analyzed the fuel for the various commonly determined parameters and obtained typical inspections from you we are interested in the additives that may be in the fuel. These may be antioxidants, Cetane Improvers, and Corrosion Inhibitors. The ultimate application for the Diesel Powered Fuel Cell which we are planning is for military application. As such the fuel must meet Military Specification VV-F-800C which contains limits and specification on the various additives. For this reason we would like to know what the types and amounts of additives might be in the fuel we tested and if Exxon DF-2 meets this specification. We would appreciate any information you can send us in this area.

Thank you

Sincerely,

  
George Steinfeld  
Program Manager

**EXXON** COMPANY, U.S.A.

200 UNICORN PARK • WOBURN, MASSACHUSETTS 01801-3390

MARKETING DEPARTMENT  
MARKETING TECHNICAL SERVICES

July 9, 1986

Energy Research Corporation  
3 Great Pasture Road  
Danbury, CT 06813

Mr. George Steinfeld

Dear George:

This is in response to your letter of June 17, 1986 and our subsequent telephone conversation of June 23, 1986.

EXXON DIESEL 2, and most commercial diesel fuels, contain additives typically like those allowed in VV-F-800C. However, specific types and amounts vary considerably. Consequently, we cannot provide specific data.

While we typically meet the requirements of VV-F-800C, we could not certify that EXXON DIESEL 2 fully complies with VV-F-800C because we do not routinely test refinery production for all of the specifications required by VV-F-800C. I would suggest that you contact the military on any concerns of testing commercial diesel fuels versus the specific requirements of VV-F-800C. From a practical standpoint, it would seem that the military would be interested in having your fuel cell capable of using commercially available fuels.

Please contact me if you have any questions.

Very truly yours,

*Bill*

W. R. Moorman  
Senior Technical Specialist

WRM/mab

ENERGY RESEARCH CORPORATION

APPENDIX 3  
WATER ANALYSIS



## YORK LABORATORIES DIVISION

### CERTIFIED REPORT TRANSMITTAL

REPORT NUMBER 30860-947  
DATE June 24, 1986

CLIENT Energy Research Corporation  
3 Great Pasture Road  
Danbury, CT 06813

ATTENTION Mr. George Steinfeld

The above referenced report is enclosed. Copies of this report and supporting data will be retained in our files in the event they are required for future reference.

If there are any questions concerning this report, please do not hesitate to contact us.

Any samples submitted to our Laboratory will be retained for a maximum of sixty (60) days from receipt of this report, unless other arrangements are desired.

Naturally, as in the past, our staff will be pleased to quote on any future requirements you may have. In addition to the service provided, we also offer the following:

- Hazardous Waste Analyses
- Product Evaluation/R&D
- Water and Wastewater Analyses
- Air and Process Gas Analyses
- Industrial Hygiene Surveys
- Metallurgical Analyses
- Microbiological Analyses
- Mass Spectrometry Services

Very Truly Yours,

Robert Q. Bradley  
Vice President

June 24, 1986

30860-947  
ENERGY RESEARCH CORPORATION  
3 Great Pasture Road  
Danbury, Connecticut 06813

Attention: Mr. George Steinfeld

PURPOSE

One water sample was submitted to York Laboratories Division of YWC, Inc. by Mr. George Steinfeld of the Energy Research Corporation. Mr. Steinfeld requested the following analyses be conducted on the sample:

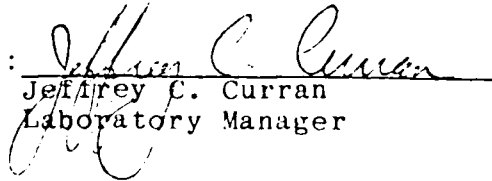
Total Solids	Bromide
Total Suspended Solids	Fluoride
Total Dissolved Solids	Iodide
Iron	Sulfide
Lead	Total Aerobic Plate Count
Tin	Electrical Resistance
Chloride	

METHODOLOGY

The sample was analyzed according to Standard Methods for the Examination of Water and Wastewater, 16th Edition, 1985; APHA-AWWA-WPCF.

RESULTS

The results are reported in Table 1.

Prepared by:   
Jeffrey C. Curran  
Laboratory Manager

JCC/md

The liability of YWC, Inc. is limited to the actual dollar value of this project.

TABLE 1  
30860-947  
ENERGY RESEARCH CORPORATION

All values are mg/L unless otherwise noted.

<u>Parameter</u>	<u>Result</u>
Total Solids	19.8
Total Dissolved Solids	19.5
Total Suspended Solids	<1.0
Iron	<0.02
Lead	<0.04
Tin	<0.4
Chloride	0.10
Bromide	<0.1
Fluoride	<0.10
Iodide	<0.5
Sulfide	<1.0
Electrical Resistance, ohms	19,900
Total Aerobic Plate Count, colonies/ml	42



## YORK LABORATORIES DIVISION

### CERTIFIED REPORT TRANSMITTAL

REPORT NUMBER 30860-651  
DATE April 9, 1986

CLIENT Energy Research Corporation  
Three Great Pasture Road  
Danbury, CT 06810

ATTENTION Mr. George Steinfeld

The above referenced report is enclosed. Copies of this report and supporting data will be retained in our files in the event they are required for future reference.

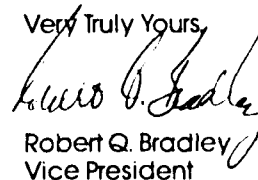
If there are any questions concerning this report, please do not hesitate to contact us.

Any samples submitted to our Laboratory will be retained for a maximum of sixty (60) days from receipt of this report, unless other arrangements are desired.

Naturally, as in the past, our staff will be pleased to quote on any future requirements you may have. In addition to the service provided, we also offer the following:

- Hazardous Waste Analyses
- Product Evaluation/R&D
- Water and Wastewater Analyses
- Air and Process Gas Analyses
- Industrial Hygiene Surveys
- Metallurgical Analyses
- Microbiological Analyses
- Mass Spectrometry Services

Very Truly Yours,

  
Robert Q. Bradley  
Vice President



April 9, 1986

30860-651  
ENERGY RESEARCH CORPORATION  
Three Great Pasture Road  
Danbury, Connecticut 06810

Attention: Mr. George Steinfeld

PURPOSE

One water sample was submitted to York Laboratories Division of YWC, Inc. by Mr. George Steinfeld of the Energy Research Corporation. Mr. Steinfeld requested the sample be analyzed for the following parameters:

Total Solids	Chloride
Total Dissolved Solids	Bromide
Total Suspended Solids	Iodide
Iron	Electrical Resistance
Lead	Sulfide
Tin	Total Plate Count

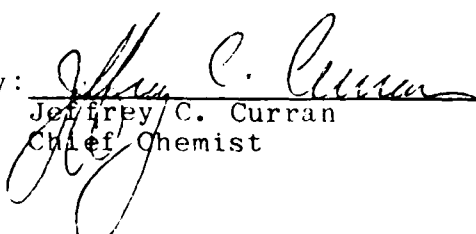
METHODOLOGY

The sample was analyzed according to Standard Methods for the Examination of Water and Wastewater, 16th Edition, 1985; APHA-AWWA-WPCF.

RESULTS

The results are presented in Table 1.

Prepared by:

  
Jeffrey C. Curran  
Chief Chemist

JCC/md

The liability of YWC, Inc. is limited to the actual dollar value of this project.

TABLE 1  
30860-651  
ENERGY RESEARCH CORPORATION  
ANALYTICAL RESULTS

(All values are mg/L unless noted.)

<u>Parameter</u>	<u>Result</u>
Total Solids	24.9
Total Dissolved Solids	24.8
Total Suspended Solids	<1.0
Iron	<0.02
Lead	<0.04
Tin	<0.4
Chloride	5.0
Bromide	0.2
Iodide	0.6
Sulfide	<1.0
Electrical Resistance	28,500 ohms
Total Plate Count	840 cfu/ml

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APPENDIX 4

PROCESS DEMONSTRATION LIST OF MALFUNCTIONS

# DIESEL FUEL PROCESS DEMONSTRATION LIST OF MALFUNCTIONS AND INCIDENTS

TEST TIME (HRS)	DESCRIPTION	CORRECTIVE ACTION	TIME REQUIRED
17	<p>Condensed moisture was flowing into the exit line because it was not all flowing into the holding tank downstream of the condenser.</p> <p>Vent gas leaving the condenser was rerouted through the holding tank while the unit was operating. Plastic line was used for a portion of the line. As it was being plumbed in with fuel gas flowing, the hydrogen ignited from the reformer burner heat when the line was inadvertently brought close to the burner. A small flame was burning at the end of the plastic line.</p> <p>This malfunction is not chargeable to the inherent design of the unit because it was due to design of the test facility only.</p>	<p>Replumb exit gas through condensate holding tank.</p> <p>The flame was extinguished with a CO<sub>2</sub> extinguisher and the line was plumbed with a steel line.</p>	2 hrs.
46.5	<p>A leak was detected between the exit of the second stage HDS and the vaporizer. The insulation was removed and a hole was found in the vaporizer inlet. The heater wire leads to the vaporizer heaters were covered with insulation which caused the wire insulation to melt and the wire to short against the vaporizer. Another leak was suspected at the pressure reducing valve by-pass valve inlet.</p>	<p>The vaporizer was replaced and fittings around the by-pass valve tightened.</p>	2 hrs.

## NOTE:

A failure/malfunction is defined as the inability to maintain desired operating conditions or development of an unsafe or undesirable condition.

# Diesel Fuel Process Demonstration List of Malfunctions and Incidents Page 2 of 4

TEST TIME (HRS)	DESCRIPTION	CORRECTIVE ACTION	TIME REQUIRED
71	<p>This malfunction is not chargeable to the inherent design because the scaled up unit will not be electrically heated. Electric heaters were only used for convenience in the test facility.</p> <p>Digital panel meter for temperature readout failed and started working again three days later.</p> <p>This malfunction is not chargeable to the inherent design because it involves a test panel instrument. The data acquisition system was recording the temperatures not readable due to the failure of the readout meter. No data was lost.</p> <p>A scaled up power plant is expected to have temperatures read directly by the controlling units. However, operator readout is desirable at times, and either better quality readouts will be required or redundancy will have to be built in for this purpose, in a scaled up unit.</p>	Unit started again with no corrective action.	0 hrs.
135	<p>The wall thermocouple on ZnO #1 shorted and gave an erroneous reading to the heater temperature controller thereby causing the heater to overheat. The over temperature was not detected immediately and caused the metal reactor to fail when pressurized. The failure was detected as a leak.</p>	The ZnO reactor was replaced with a spare. The t/c wire was replaced.	10 hrs.

TEST TIME (HRS)	DESCRIPTION	CORRECTIVE ACTION	TIME REQUIRED
	<p>This malfunction is only partly chargeable to the inherent design because electrical heaters will not be used to heat the HDS or ZnO in a larger unit. However, failure of thermocouples for readout and control purposes can be a problem. A recommended design modification is to provide double thermocouples at each location so that if one fails, the other can be utilized until the thermocouple can be replaced.</p> <p>A leak was detected upstream of the pressure reducing valve by-pass valve.</p> <p>This malfunction, although typical of this type of test unit operating at pressure, is a design problem. It is recommended that larger scale units be designed with backwelded fittings to avoid leaks.</p>	<p>The leak was repaired by replacing a fitting.</p>	2 hr
182	<p>During week-end cooldown approximately 2000 gm of fuel was sucked into the HDS system as the system was cooling down.</p> <p>This malfunction is chargeable to the design of the system and can be corrected by the action specified.</p>	<p>A valve was put in the fuel line to isolate and vent the fuel supply during cooldown.</p>	1 hr.
255	<p>After replacement of the ZnO bed a leak was found at the ZnO exit sample tap. In addition vapors were observed from the top of the second stage HDS.</p>	<p>The sample tap cap was tightened. Insulation and heaters from the first second stage HDS were removed and the reactor inspected for leaks. The exit fitting gasket was found to be loose. The gasket was replaced and fitting tightened.</p>	4 hr

TEST TIME (HRS)	DESCRIPTION	CORRECTIVE ACTION	TIME REQUIRED
	<p>This malfunction is only partly chargeable to the design of the system since sample taps may not exist in the full scale unit. However, leaks in general are a problem and can be corrected by backwelding all threaded fittings as mentioned previously.</p>		
373	<p>During 1/2 flow tests, the diesel fuel pump was turned down to 10% of its total flow capacity, and stopped pumping fuel at one point due to loss of prime.</p> <p>This malfunction is not chargeable to the design of the system since the full scale unit will have pumps sized for the actual flows expected. The pump used in this demonstration test had a flow capacity larger than required and a turn down to 10% of maximum.</p>	Fuel flow rate was increased temporarily to recover its prime.	1/2 hr



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